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STUDIES IN THE GROWTH OF GRAPES.

by

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During the grape season of 1922 in South Africa the question of the ripeness of grapes arose in connection with their export. In this country the export regulations with regard to grapes stipulate that "no unripe grapes will be passed by the Inspector", while the general regulations concerning fruits for export provide that "all fruit shall be in a sound condition, fully developed and not too unripe." In America a legal standard has been set up whereby the sugar content of the juice must be at least 16 - 17° Balling according to the variety of the grape (10). This law was framed to prevent the indiscriminate marketing of green immature grapes and has apparently proved successful in practice.

In view of the indefinite nature of the terms "ripe" and "unripe", it is clear that any attempt to apply regulations, involving such terms, must be an entirely arbitrary proceeding depending to a large extent upon the personal interpretation of such factors, and consequently will undoubtedly be subject to considerable variations. The problem of what constitutes a ripe grape must therefore be solved before an attempt can be made with any chance of success to apply regulations which involve an estimation of the degree of ripeness of the fruit. Since sweetness is a desirable quality in any fruit, attention is generally focussed upon the sugar-content, more especially as the flavour appears to be associated with this factor. At the same time it is important to remember that the intensity of a sensation such as sweetness is considerably modified by the presence of an acid or sour substance (36). It is, therefore, clear that the condition of ripeness of a fruit must also depend upon the acidity of the juice. It may be concluded that a high sugar-content and a low acidity are

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desirable for the production of a mild sweet flavour in the fruit.

At the present time there is no generally established method for determining when grapes have reached a condition suitable for export. In addition to the taste which may be subject to wide variations, the colour, firmness and size all influence the picker's decision. When the appearance and attractiveness of the product are to be considered the physical aspect of the berry must be given due weight, but the final decision regarding the maturity of the fruit must depend essentially upon the quality and flavour of the juice. In order to obtain an idea of the limits of some of the factors which influence "the condition of ripeness" in connection with table varieties of grapes, an investigation into the changes which occurred during the ripening of grapes was undertaken. Preliminary work was carried out during the 1923 season and the work was continued during the 1925 and 1926 seasons in order to determine the extent to which these limits are affected by seasonal conditions. In 1927 similar work was carried out for the purpose of studying the effects due to a variation in locality.

A great many analyses of different varieties of grapes have been made both by American and by European investigators, but most of the work has been mainly concerned with the final crop yield, and such analyses do not show the progressive changes in composition occurring during the process of ripening. The changes have been studied for American varieties by Alwood and his associates[1], by Bioletti, Cruess and Davi[5] and by Noyes, King and Martsolf[28]. The European varieties have been studied by, amongst others, Brunet[8] and by Baberon and Changeant[4] in France, by Kelhofer[21] in Italy and by Baragolia and Godet [3] in Germany. Lewis[26] has published a paper dealing with the development of the grape in South Africa, but his work was confined to those varieties of grapes which were suitable for wine-making and the question

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was investigated mainly from this point of view. In none of these investigations, however, has an attempt been made to develop any theoretical concept of the changes which occur during ripening. The present discussion will deal mainly with this aspect of the problem.

In order to study the progressive changes which occurred during the ripening process of grapes, the analyses were performed at weekly intervals during each of the periods of investigation. The varieties of grapes employed in this work have all been what might be termed "table grapes" since the problem in the first place arose in connection with this type of grape. In the 1923 season the samples were obtained from the Government Wine Farm, Groot Constantia, during the period 31st January to 28th March. Four varieties of grapes were employed, namely, White Hanepoot, Red Hanepoot, Barbarossa and Flaming Tokai. The work was continued for as long a period as possible until finally the exigencies of the vintage precluded further work. In this work there has been no attempt to study the changes which may have occurred <u>after</u> full maturity had been reached. At this stage in all cases the grapes were consigned to the press. During 1923 the work was of a preliminary nature and was carried out at the Government Wine Farm, Groot Constantia, so that rapidity was the essential factor in the methods adopted owing to the limited facilities and time available for the work. During the remaining seasons the analytical work was all performed in the Government Laboratories, Cape Town, so that the analytical work was not subject to any limitations in the matter of available facilities. In these cases the samples were forwarded to the Laboratory at weekly intervals and the analyses performed immediately on arrival. In the 1925 season the work was carried out during the period 28th January to 11th March and six varieties of grapes from Groot Constantia were studied. In addition to the four varieties studied in 1923 two further varieties were employed, namely, Gros Maroc and Waltham Cross. In the 1926 season the

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same six varieties were forwarded from Groot Constantia and studied during the period 13th January to 24th March. The results of these investigations, embodying the analytical data, have appeared in the form of Government Bulletins[11,12,13]. It soon became apparent that for practical purposes the determinations could be confined to the estimation of sugar, acid and soluble solids in the juice and total solids in the berry. In 1926, therefore, the analyses were confined mainly to these factors although determinations of tannin and the conductivity of the juice were also made. During the 1927 season work was carried out on grapes which were obtained from the Government Viticultural Station at Paarl in order that the effect of changes in locality might be studied. In order to obtain a clearer idea of the initial stages of growth than had previously been possible, the work was commenced as early in the season as convenient and covered the period 1st December, 1926, to 29th March, 1927. In this case three varieties only were employed, namely, White Hanepoot, Barbarossa and Flaming Tokai. These varieties were chosen as being representative of the six varieties previously employed. For all practical purposes White and Red Hanepoots may be considered as identical so far as characteristic properties are concerned. This can be seen by reference to the data given in the present paper. Dr Perold[29] in his book on Viticulture states that these two varieties are identical in all respects except colour. He regards the Red Hanepoot simply as a "bud variation" of the White variety.

The Government Wine Farm, Groot Constantia, is situated on the lower eastern slopes of Table Mountain, about three miles from the coast. The samples obtained from this locality were picked in the early morning and immediately forwarded by rail to Cape Town. These samples arrived at the Laboratory in Cape Town on the same morning and the analyses were at once started. The Government Viticultural Station at Paarl is situated on the slopes of the Paarl Mountain, and has an easterly aspect. Paarl lies about thirty five miles in an

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easterly direction from Cape Town. The samples obtained from this station were picked during the morning and were forwarded by rail to Cape Town during the same day. The samples arrived at the Laboratory in the afternoon and the analyses were commenced the following morning. In all cases the samples were taken at weekly intervals during the period of investigation.

At the present time there is no method of estimating quantitatively all the elements which enter into a determination of the ripeness of a fruit. Not only are sugar and acids concerned but the texture, aroma and minute quantities of flavouring substances are also involved. In the case of plums, Diehl and Magness[16] have found that the sugar content is closely associated with the other constituents which determine the quality of ripeness and is therefore a measure of this quality. Since in all fruits the flavour, depends principally upon the content of sugar and acids, it seems probable that the same conclusion should be of general application and, more particularly, in the case of grapes where the greater portion of the "soluble solids" in the juice consists of sugars. Naturally variations dependent upon conditions such as climate, soil, aspect of the vineyard, etc., must occur, but these will not be sufficiently great to vitiate the general argument. It is perfectly clear that determinations of the content of sugar and acid are essential factors in the study of the ripening of fruits. Since fruits, when subjected to pressure, yield a juice which contains the principal portion of their palatable constituents, a study of the sugar and acid content of the juice is an important aspect of an investigation of fruits.

In the Bulletins referred to, it has been shown that the most important changes which occur during the ripening of grapes are those which take place in the sugar and acid content of the juice. The increase in the weight of the berry is mainly due to the increase in the sugar content and, obviously, a similar conclusion applies to the changes in

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the soluble solid content of the juice. It is obvious that, from the point of view of the picker, the average weight and average volume of the berries are important aspects of the problem, but the physical character of the berry forms in itself a very unreliable guide as regards the condition of ripeness. Factors, such as climate, soil, lay-out of the vineyard, thinning of the bunches, will so affect the appearance of the berry that correct conclusions based upon the physical aspect alone must be a matter of considerable practical experience allied to a thorough knowledge of local conditions. Such methods of judgment may be regarded as entirely empirical. It was shown in the results for 1923 and 1925 that the changes in volume of the berry were closely related to the changes in weight. Determinations of the yield of juice were shown conclusively in 1926[13] to be of little value in following the course of ripening. The amount of juice obtained on pressing the berries was subject to such great variations on account of the variable pressure used that the results afforded no criterion of the actual amount of juice present. The determinations of the nitrogen content of the berry yielded values which were small in magnitude and subject to irregular variations which could not be definitely correlated with the changes due to ripening. The ash in the berry has also been determined, but no attempt has been made to incorporate the data into the present discussion. During the 1925 season work was done in relation to the properties of the seeds but, since such data do not possess any practical value in determining the condition of ripeness, this portion of the work was not continued. For these reasons the present discussion will be confined to the changes which take place in the acid, sugar and soluble solids in the juice and the total solids in the berry.

In general the methods of procedure have, as far as possible, been maintained unaltered during the different periods of work. Ten bunches of each variety of grape were

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forwarded for analysis and from these bunches average samples of the berries were obtained as required. To obtain a sample of juice a sufficient number of berries were taken at random from all the bunches to yield at least 250 c.c. of juice. The juice was expressed either by means of a small fruit press or by hand and then filtered through linen into a measuring cylinder. The juice was then allowed to stand until the suspended matter had settled. The reading of the Balling hydrometer and the temperature of the juice were then determined. As a check upon the Balling reading the density of the juice was also determined. In 1923 this latter operation was performed by means of a hydrometer; in 1925 and 1926 a Westphal balance was used for the same purpose, while in 1927 the density of the juice was determined by first filtering the juice through filter paper and then using 50 c.c. specific gravity bottles. The Balling reading and the density were then corrected to 20°C and the latter quantity converted into grams of soluble solids per 100 c.c. of juice by means of tables. In 1926 the "soluble solids" in the juice was estimated by evaporating 25 c.c. of the juice on a water-bath and finally heating to dryness in an electric oven at 100°C. The results so obtained were found[13] to give values which agreed fully within the limits of error with the values obtained from the density readings. The acidity of the juice was determined by titration. 10 c.c. of the filtered juice was diluted with distilled water and titrated with $^{N}/_{10}$ alkali using phenolphthalein as indicator. The results were calculated in terms of grams of tartaric acid per 100 c.c. of juice. The sugar content of the juice was estimated during the 1923 season by Benedict's method, but in all the later work the method of Lane and Enyon[25] was adopted in which Fehling's solution was used with methylene blue as an internal indicator. This method has been found to be entirely satisfactory - the end-point is distinct and readily detected. The juice was diluted and clarified with saturated /

saturated lead acetate solution. An aliquot portion of the filtrate was treated with potassium oxalate to remove excess of lead. The results were calculated in terms of grams of invert sugar per 100 c.c. of juice. A large number of experiments have shown that cane sugar is absent or present in such small quantities that it has no effect upon the changes in sugar content of the juice. The "total solids" in the berry was determined by halving a sufficient number of berries and using one half only of each berry for the estimation. The loss in weight was estimated by placing the dish in an electric oven at $100^{o}C$ for 24 hours. Independent experiment had shown that after this period there was, in general, a small but constant rate of loss of about 0.05% per hour. The regularity of this loss was concluded to be due to the commencement of decomposition of carbohydrate material, more particularly the sugars, present in the berry. On this account, 24 hours was chosen as the standard time of heating under these conditions. The same experiment had shown that this method wasapplicable to all the varieties. The results were then expressed in terms of residue per 100 grams of berry. In connection with the methods adopted for other determinations reference may be made to the published Bulletins[11,12,13].

Owing to the fact that during the seasons of 1923, 1925 and 1926 the samples were all obtained from one locality, namely, Groot Constantia, the results are strictly comparable for the different seasons, and the effects due to variations in seasonal conditions can be studied. In 1923 no rain fell during the period of investigation and the days remained clear and warm. Under such conditions a high sugar content and a low acidity would be expected. In 1925 the total rainfall during the period under review was only 0.21 inches and this occurred on two days about a week apart near the beginning of the ripening period. In both these years, therefore, the conditions were apparently favourable for photosynthesis. In 1926 the total rainfall was 2.10 inches and this was distributed over seven days during the investigation.

investigation. There were also a large number of cloudy days and the mean temperature was lower during 1926 than during 1925. The conditions, therefore, were not so favourable to plant development as during the previous seasons. On this account the period of ripening was prolonged and the attainment of maturity somewhat delayed. On the other hand, in 1926 the analyses were commenced about three weeks earlier than in previous seasons so that a more complete record of the ripening period was obtained. In connection with the effect of climatic conditions upon the growth of grapes a paper(9) dealing with "Some Effects of Seasonal Conditions upon the Chemical Composition of American Grape Juices" is of considerable interest. Somewhat marked variations are recorded in the composition of different varieties of grapes for different seasons. It is also stated that "there is a consistent and fairly high degree of correlation between the sugar, acid and total astringent content". It is, therefore, clearly important that, when comparing the results for different seasons, the grapes should be at the same stage of maturity. In the above paper, however, there seems to be little connection between the season and date of picking. The conclusions are, therefore, open to objection on this ground. In order to compare the effects due to a change in locality the work was continued along the same lines in 1927 with grapes from Paarl. It was intended to carry out parallel investigations on grapes from both Paarl and Groot Constantia, but circumstances unfortunately prevented the obtaining of samples from the latter locality. However, as will be shown later, the variations in the factors for the samples from Constantia for the three seasons 1923, 1925 and 1926 lie within fairly narrow limits so that their mean values form a very useful basis for comparison. In 1927 the total rainfall at Paarl during the period of the investigation was 3.03 inches of which 2.38 inches fell during February (mainly about the middle of the month). The average temperature during the same period was considerably higher than that which is usual at Constantia. The season

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on the whole was an unfavourable one from the grape growers' point of view. At the beginning of the season the weather was hot and dry and it was only about the middle of February that sufficient rain fell to mitigate somewhat the ill-effects of the preceding dry weather.

In order that the analytical data may be more readily studied and the course of the changes made more apparent the results have, whenever possible, been presented in the form of curves. Owing to the almost insuperable difficulties of obtaining absolutely representative samples from a product so widely variable as a fruit, it would not be expected that the analytical data would lie completely on a smooth curve. However, in order to simplify the data and render the changes clearer, it has been decided to draw smooth curves and regard the irregularities as due to experimental errors. The curves so obtained represent closely the changes which occur during the ripening of the fruit. Apart from the difficulties of obtaining representative samples, even from a given batch of fruit such as grapes, there are factors which are quite as important as the method of sampling. In this connection the work of Bioletti, Cruess and Davi[5] is significant. These workers point out that considerable irregularity occurs from week to week. They show that young vines ripen more rapidly than mature vines and samples should therefore be taken from vines of the same age. The position of the bunch on the vine affects the composition of the fruit. Bunches on the side of the vine most exposed to the sun and bunches near the tip of the vine ripen more rapidly than those on the shady side and lower down on the vine. Even when these factors are taken into account there is still some variation in the Balling degree of the juice from bunches of similar appearance and size, from the same vineyard on the same date. In addition the position of the berries on the bunch affects the composition of the fruit. The degree of pressing, however, appeared to have no effect upon the analytical results. These facts show how difficult it is to select grapes which

which will represent a truly average sample of the crop. Errors due to the various sources mentioned would be extremely difficult to eliminate and the smoothed curves may therefore be regarded as being fully justified in view of the difficulties involved.

It has been found that the changes in the total solids and in the soluble solids follow closely the changes in the sugar content. During the development of the grape two very distinct periods are apparent. During the first period the acidity of the juice increases to a maximum value. After this point has been reached the acidity commences to decrease. The rate of decrease becomes less as maturity is approached until finally a practically constant minimum value of the acidity is attained. During this second period the berry ripens rapidly. During the initial period the sugar content of the juice is small but later, during the second period, the sugar increases rapidly. As maturity is approached the rate of production of sugar becomes less until finally, at maturity, the amount of sugar becomes nearly constant. The first period has been termed "the initial growing period" and the second stag of growth may be termed "the ripening period". Lewis[(26)] makes the statement that "the acidity increases to a maximum and the point of maximum acidity agrees closely with the increase in sugar and the appearance of laevulose, i.e., with the beginning of the ripening period". This stage in the development of the grape is marked by many signs of change in the appearance of the bunches. This is the point in the development of the fruit to which the French apply the term "veraison". In the results for 1923 and 1925 this stage was not apparent in the data since the investigations were not commenced until this point in the development of the grape had been passed. In the 1926 results this point was clearly defined but the data were not sufficient to allow any conclusions to be drawn regarding the nature of the changes which occurred during the "initial growing period". On account of the very early com-

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commencement of the work in 1927 sufficient data have been collected to enable some idea to be formed of the course of these initial changes.

Since growth is obviously a dynamic process it follows that some relationship must exist between the changes in the magnitude of the factors involved, their final magnitude and the total time of growth. The value of employing some form of equation to express the changes which occur during the ripening of fruits is largely dependent upon the possibility of employing the constants obtained in this way for the purpose of expressing quantitatively the resultant effects of the conditions of growth. The type of equation to be chosen will therefore be one which most suitably fulfills this condition while, at the same time, agreeing closely with the experimental facts. Such an equation need not necessarily be regarded as giving a complete picture of all the intricate processes involved in the growth of the organism. The criterion of the value of a mathematical expression may be regarded as the test whether, or not, it serves any useful purpose.

So far as the changes in acidity are concerned an early attempt [14] was made to express the change of acid with time by means of a simple logarithmic function of the form $x = ke^{-bt}$. It was found that this gave a fairly close approximation, at least, during the period of ripening, but that as the grapes approached maturity the calculated curve became too steep while the experimental curve began to flatten out. This might be expected since the value of the acidity tends to reach a constant minimum value at maturity. This function is, therefore, only capable of application over a limited period. This was very clearly seen during the 1926 season when an attempt was made to predict the acidity by means of this expression. The more extended period of the investigation brought out clearly the discrepancy which arose as maturity was reached. For this reason this simple form of the logarithmic expression has been abandoned and an

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expression evolved which gave values more in accordance with the experimental data and covering the entire range of the ripening period.

In connection with the laws of plant growth Blackman[6] has evolved what may be termed "the compound interest law of growth". This may be expressed symbolically in the form $W_1 = W_0e^{rt}$ where "W_0" is the initial weight and "W_1" the final weight of the plant in time "t". "r" is termed the efficiency index and is regarded as representing the efficiency of the plant as a producer of raw material. The value of "r" is naturally affected by external conditions but, while there are variations for different plants, the index is, to a large extent, regarded as characteristic of different species and varieties. Since "r" is related simply to the initial and final weights of the growth cycle, it is clear that the value is only an average for the whole cycle and yields no information regarding the actual course of the growth changes. If "r" were a constant throughout the cycle it follows that growth would continue with an increasing rate during the whole period. The expression would not be applicable when the growth begins to fall off. In a paper on the significance to be attached to this index Kidd, West and Briggs[22] show that the value of "r" is not a constant and has no value in comparing the efficiency of plants except over strictly comparable times and phases of development. These workers have made a study of the growth changes in the maize plant[23] in which they have adopted the "weekly growth rate" as a means of comparison. However, when the changes in the growth rate are studied during the development of the whole plant, it is found that the formation of the flowers and seed introduce subsidiary changes which directly influence the growth rate. In the development of a fruit there are no secondary changes to be taken into account so that the problem is somewhat simplified.

A similar type of expression to the "compound interest law" has been developed more fully by Mitscherlich[27]

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in connection with the factors which limit crop yield. His ideas may be summed up by saying that "the increase of a crop produced by unit increment of the lacking factor is proportional to the decrement from the maximum", and may be expressed in the form

$$\frac{dy}{dx} = k(a - y)$$

or

$$\log (a - y) = c - kx \quad \text{i.e.} \quad y = a(i - e^{-kx})$$

Thus, as the factor "x" increases, the yield of "y" tends to increase to the maximum value of "a". This equation is of the type of a unimolecular reaction in which the rate of change decreases from the commencement of the reaction.

Mitscherlich's expression also has been criticised by Briggs[7], but the main ground of criticism seems to be based upon the fact that the changes can be equally well expressed by means of different mathematical functions such as $y = a + bx + cx^2$, and $y = A \frac{x}{x+c}$. Briggs also points out that Mitscherlich has been inclined to strain the flexibility of his formula by attributing values to the constants which are not in the best accordance with the experimental data. On the other hand, formulae such as suggested by Briggs do not bring out clearly the significance to be attached to the constants employed. In the present case the use of this formula was not possible on account of the fact that there is an initial lag in the rate of change of the sugar, soluble solids and total solids.

In practice it has been found that growth begins slowly but goes on at an increasing rate until the products of growth have accumulated appreciably, after which the rate of growth slows down. These changes are characteristic of an autocatalytic reaction and the smoothed time curve of the change is sigmoid in form. It has been shown that in many cases the time curves of plant growth exhibit this general reverse curve of an autocatalytic reaction. Robertson[34], in particular, has developed this type of equation, more

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especially in respect of its application to the growth of animals. The equation takes the form

$$\log \frac{x}{a - x} = K(t - t_1)$$

Robertson stresses the fact that the very evident complexity of the growth processes constitute an obstacle to the acceptance of such a simple expression. At the same time he makes use of the idea that the complete process of growth during any given cycle is dependent upon some "master reaction" which admits of representation by the autocatalytic equation. Probably each autocatalytic cycle of growth represents the fusion of very many different autocatalysed processes, but such a fusion is contingent upon the presence of a catalyst which is common to all the processes. For example, Gregory[19] has shown that the changes in lengths and areas of the leaves of Cucumis sativus may be expressed very closely by means of this formula. Prescott[30] has employed this form of equation to express the flowering curve of Egyptian cotton. This author points out that an analysis of the curves obtained should indicate the existence of disturbing factors upon the yield of the plant. In a paper by Gaines and Nevens[18] the use of what might be termed the "Robertson equation" has been fully worked out in the case of the changes occurring during the growth of the sunflower and of maize. In this case the authors have followed the idea developed by Robertson and have attempted to explain the deviations from the normal course of the autocatalytic curve during the later stages of growth by supposing that the changes in the growth rate are due to the fusion of two separate autocatalytic cycles. In this way the changes due to the formation of the flowering portions of the plants are accounted for. The growth of the fruit of a plant probably represents in itself a separate autocatalytic cycle. As an example of this, Anderson's data[2] on the growth in weight of the fruit of Cucurbita pepo have been shown by Robertson to follow closely the simple autocatalytic growth equation. Reed and Holland[33] have

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measured the growth of sunflowers (Helianthus) at weekly intervals and have made a close study of the applicability of the autocatalytic expression to the growth changes.

In the present work this type of expression has been found very suitable for expressing the changes in the sugar content of grape juice and, with a slight modification, the changes in the soluble solid content of the juice and in the total solids in the berry. The study of the changes which occur in a particular portion of a plant, such as the berry, eliminates the occurrence of subsidiary changes due to morphological considerations and the problem of expressing the changes in some definite form is rather simplified. If the constants in the autocatalytic equation have the values attached to them bt Robertson they should be of value in supplementing the data of crop-yield and emphasizing the differences between the different varieties. It was finally found that an expression closely resembling Mitscherlich's and very similar to the simple logarithmic function was applicable to the changes in the acidity of the juice. In both these types of equations it has been found that the constants possess a definite significance which it would be idle to ignore.

In regard to the changes which occur in the other factors which have been examined, various considerations have precluded their detailed study. The average weight of the berry did not yield any further information then had already been gained. The growth changes of the mineral constituents do not conform to the time relations indicated by any simple expression such as the autocatalytic formula, and it would appear that their concentration in the berry is determined by quite other factors then those which determine the rate of growth of the acid and sugar. Determinations of the nitrogen contents of the berries were highly irregular. Priestley and Wormall[31] make the suggestion that the organic nitrogenous substances present in the sap of the vine are so minute in quantity that their role in relation to growth must be confined

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either to catalytic action as enzymes or to growth regulation as hormones. Since the total nitrogen in the berry is approximately .06 - .07 %, it is possible that a similar conclusion may be valid in this case. Determinations such as weight of seeds, volume of juice, possess in practice no great value.

The present discussion, so far as the theoretical treatment of the growth changes is concerned, is, therefore, confined to a study of the changes in the acidity, sugar and soluble solid content of the juice, together with the changes in the total solids in the berry. For the sake of convenience the subject matter has been divided into sections.

(a) SUGAR CONTENT OF THE JUICE.

On examining the curves obtained for the changes in the sugar content of the juice it was readily seen (particularly in the case of the results for the 1926 and 1927 seasons) that any modifications of the expression, which had been developed for the changes in acidity, were not applicable to the sugar curve. It was clearly evident from the curves that there was an initial lag in the rate of production of sugar. An expression such as Mitscherlich's, which presupposes a high initial rate of production, or one which demands a final rapid production, would both be unsuitable. A curve of the former type would necessitate far too short a growing period. The type of curve, obtained in practice, was the general reverse curve which is characteristic of growth in plants and animals. In these cases the growth of organism takes place at first slowly, later with increased velocity and finally as slowly as it began. Such a process resembles the course of an autocatalytic reaction. The changes in growth can be most suitably expressed by the equation for such a reaction. Robertson[34] has developed this idea and applied this form of equation particularly to the case of the growth of animals. The lead thus put forward has been followed by a number of workers. This type of equation has been found to express very closely

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the changes which occur in the sugar content of grape juice, and the constants should be extremely useful in the study of the crop.

If the amount of material to be transformed be represented by "b" and the amount actually transformed in time "t" be "x", then the amount remaining to be transformed is "b - x."

The velocity of the reaction is proportional to "b - x" and is also catalysed by a porduct which is proportional to "x." The velocity of the reaction is therefore

$$\frac{dx}{dt} = kx(b - x) \text{-----------------------} (1)$$

where "k" is the velocity constant of the reaction. It is clear that the rate of the reaction will increase with time to a maximum value when $x = b - x = \frac{b}{2}$ after which the velocity will decrease. By integration of (1)

$$\log \frac{x}{b - x} = K(t - t_1) \text{-------------------} (2)$$

where $K = kb$ and $t = t_1$ when $x = \frac{b}{2}$. "t_1" is the time in which "b" is half transformed and may be regarded as the "half-value period".

In this latter form the equation is applicable to observed data. In the general form of the curve there are two asymptotes, one at "O" and the other at "b". Robertson's arguments in favour of accepting such a simple expression to represent the changes which occur during growth have already been briefly mentioned. In regard to the significance to be attached to the constants "b" is the final resultant of the growth processes and, according to Robertson, is subject to a considerable degree to modification by external conditions. On the other hand "k" is regarded as a specific constant representing inherent qualities of growth. Since K = kb, the value of "k" may be determined from the values of "K" and "b" as obtained by observation. Robertson infers that the value of "k" is a constant which is independent of environment and represents an internal rather than an external character of growth. Reed and Holland(33) maintain that the rate of growth in the Helianthus is controlled by some internal factor or factors which are of such importance

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that the effects due to external factors are overbalanced, provided that the latter do not approach too closely the maximum or minimum values. This view cannot be regarded as entirely correct. In the first place their investigation was confined to the study of one variety of Helianthus and in the second case their statement regarding the external factors is equivalent to specifying a given set of conditions. In such circumstances a constant value of "k" would be expected. Kidd West and Briggs[23] maintain that external conditions, in addition to causing modification in the morphological changes in the general form of the growth rate curve, must directly affect the absolute value of the growth rate. The results which have been obtained in the case of grapes bear out this view. Gregory[20], dealing with the growth of barley, brings out the important point that the different physiological processes making up plant growth are differently affected by changes in external conditions and thus tend to compensate one another. At the same time he concludes that, although the order in which the different changes take place is governed by internal factors, the effect of environment is reflected in the changes in the values of the growth rates, by a shift in the points of inflection and by a change in the end points. From the point of view of chemical dynamics variations of "k" with external conditions would be expected. Prescott[30] in his paper gives figures which show that "k" is subject to variation according to external conditions.

In practice attention is generally focussed upon the final growth attained by the crop and in general this is identical with "b". From the relationship K = kb it is apparent that the constant "k" varies in an inverse ratio to the crop yield. A high value of "K" means a short growing period and, as such, tends to be associated with a low crop yield. Since "k" is directly proportional to "K" the value of the former must vary in the same way. In these circumstances it may therefore be expected that conditions which affect the

crop /

crop yield will also cause variations in the values of "K" and "k". "k" may be regarded as a constant representing the <u>growth velocity</u> of the plant or organism under the conditions of experiment. Co Conversely "$^b/_k$" varies directly with the crop yield and is therefore somewhat better adapted for purposes of comparison. In this form it is a constant representing the <u>growth capacity</u> of the plant. Its value as an index of capacity depends upon the association between the length of the growing period and the final extent of growth. It represents the inherent capacity for crop yield and should serve as a useful means of comparison between different varieties of plants under comparable conditions. Since the growth rate of a plant varies with the age of the plant as well as with the seasonal conditions, it would not be expected that these quantities would be absolutely constant under all conditions. Consequently they should possess some value as a measure of these variables and in crop studies these data should possess a practical significance.

The results of the analyses of the sugar content of the juice are given in Tables I - IV. The sugar is expressed in terms of invert sugar per 100 c.c. of juice. The locality from which the grapes were obtained is indicated by the use of the place names as adjectives.

<u>TABLE I</u>.

<u>Constantia Grapes pressed in 1923</u>.

<u>Date</u>.	<u>Red Hanepoot</u>.	<u>Barbarossa</u>.	<u>Flaming Tokai</u>.
31. 1.23	10.26	-	-
7. 2.23	15.00	12.50	11.94
14. 2.23	13.93	10.96	14.63
21. 2.23	16.81	11.33	13.60
1. 3.23	18.28	13.29	14.03
7. 3.23	19.50	17.20	19.34
14. 3.23	20.01	16.24	19.26
21. 3.23	22.89	16.52	19.29
28. 3.23	24.94	18.86	20.53

TABLE II. /

TABLE II.

Constantia Grapes pressed in 1925.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28. 1.25	7.02	7.69	3.78	4.23	7.54	2.98
4. 2.25	8.36	10.60	8.00	7.95	8.67	8.83
11. 2.25	13.27	13.38	12.06	10.41	11.92	10.99
18. 2.25	15.01	15.63	11.97	11.84	14.97	15.23
25. 2.25	17.99	16.60	14.30	15.90	18.99	15.09
4. 3.25	18.48	19.12	17.50	16.24	15.93	17.24
11. 3.25	19.22	18.83	17.45	17.20	15.87	19.82

TABLE III.

Constantia Grapes pressed in 1926.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
13. 1.26	1.55	1.55	1.33	1.41	4.87	0.93
20. 1.26	3.68	2.78	1.36	1.82	5.20	1.19
27. 1.26	7.93	7.63	1.80	1.70	7.96	3.21
3. 2.26	9.98	10.49	3.18	4.36	9.86	4.95
10. 2.26	10.75	11.74	6.58	9.24	13.16	7.16
17. 2.26	14.74	14.67	8.70	11.12	12.67	8.90
24. 2.26	16.66	16.87	12.65	13.80	14.24	12.49
3. 3.26	18. 03	19.08	13.49	14.91	17.93	14.61
10. 3.26	21.52	19.55	15.33	16.48	19.60	16.01
17. 3.26	19.83	18.47	15.80	17.39	-	15.45
24. 3.26	21.66	20.84	15.40	-	-	16.86

TABLE IV /

TABLE IV.

Paarl Grapes pressed in 1927.

Date.	White Hanepoot.	Barbarossa.	Flaming Tokai.
30.11.26	0.49	0.57	0.38
7.12.26	0.91	0.88	0.73
14.12.26	1.00	1.05	0.79
21.12.26	1.17	1.08	0.97
28.12.26	1.28	1.19	0.87
4. 1.27	2.72	1.32	0.94
11. 1.27	3.63	1.66	1.27
18. 1.27	6.10	2.16	4.33
25. 1.27	8.88	3.10	5.21
1. 2.27	11.74	4.56	9.16
8. 2.27	12.71	7.92	10.11
15. 2.27	16.44	14.06	13.56
22. 2.27	16.23	14.96	11.94
1. 3.27	20.25	17.02	14.01
8. 3.27	20.38	15.93	14.91
15. 3.27	21.07	17.43	15.80
22. 3.27	22.92	18.86	17.53
29. 3.27	23.24	19.00	17.64

In the case of the values for Red Hanepoot in 1923 the last two values have not been used in computing the theoretical curves as there seems to be some evidence that these results are due to abnormal shrinking of the berry at the end of the period of maturity.

In calculating the constants the time has been reckoned in days from the commencement of work as origin in each season. The approximate constants obtained from the curves have been corrected by the method of least squares and logarithms to the base 10 were used. The constants so obtained from the experimental data are given in Table V.

Table V /

TABLE V.

Sugar _ $\log \frac{x}{b - x} = K(t - t_1)$.

Locality.	Variety.	Year.	b	K	t_1
Constantia.	White Hanepoot.	1925	20.25	0.0392	8.0
		1926	21.82	0.0383	26.0
	Red Hanepoot.	1923	20.40	0.0383	0.5
		1925	19.85	0.0385	5.5
		1926	21.05	0.0373	25.5
	Gros Maroc.	1925	18.45	0.0435	11.5
		1926	16.10	0.0427	31.5
	Barbarossa.	1923	17.10	0.0430	4.0
		1925	17.85	0.0447	11.0
		1926	18.10	0.0427	31.0
	Waltham Cross.	1925	20.00	0.0358	8.0
		1926	19.50	0.0347	21.0
	Flaming Tokai.	1923	19.60	0.0462	5.0
		1925	18.70	0.0466	11.0
		1926	17.00	0.0435	31.0
Paarl.	White Hanepoot.	1927	24.42	0.0258	68.5
	Barbarossa.	1927	19.50	0.0324	74.0
	Flaming Tokai.	1927	18.25	0.0303	70.5

When these expressions are plotted in the form of curves it will be seen that there is a very close agreement between the observed and calculated values. For the sake of clarity and convenience, and on account of the greater number of varieties employed, the curves for the 1926 season only have been given (see Fig.1). The results for the remaining seasons are similar to those given. The mean deviation from the theoretical values for the six varieties for the 1926 season is $\pm$ 0.63, and the standard error of the mean value of the sugar distribution is $\pm$ 0.97. It may therefore be concluded that the deviations are not significant.

On account of the relatively short period during which the experiments were conducted in 1923 and 1925 the

initial /

initial lag in the production of sugar is not apparent but the form of equation has been assumed to be the same as for the 1926 and 1927 results, the constants being calculated on this assumption. The initial slow increase in sugar and the final decrease in the rate of production of sugar can be clearly seen in Fig.1.

In the case of the values of "t_1", the time when half the final amount of sugar has been formed, these have been calculated from the time of commencement of the observations in each season. Since this varied with each season the values of "t_1" are only comparable amongst themselves for a given season. The data for 1923 have been introduced into the tables but, owing to the difficulties under which the work was performed, the results may be regarded as approximate. When the values of the "half period" "t_1" for 1925 are compared it will be seen that this stage is reached in 8.0, 5.5, 11.5, 11.0, 8.0, 11.0 days for the varieties in the order given in the table. These figures indicate that the six varieties may be clearly divided into two classes which may be distinguished by the terms early- and late-ripening varieties. The first class, including the two Hanepoot varieties and Waltham Cross, reach the "half period" at an earlier date than the remaining three varieties. In 1926 the values of "t_1" were 26.0, 25.5, 31.5, 31.0, 21.0, 31.0 days for the six varieties in the same order. The same order of division is again manifest but the early ripening characteristics of Waltham Cross are more clearly evident. In 1927 the values are 68.5, 74.0 and 70.5 days for White Hanepoot, Barbarossa and Flaming Tokai respectively. These results in themselves do not indicate any essential difference between Paarl and Constantia grapes but, if the actual dates were compared, it would be found that the grapes ripen slightly earlier at Paarl than at Constantia.

In the equation adopted, "b" represents the final yield of sugar and it will be seen from Table V that this value depends upon the variety of grape. The Hanepoots are

characterised /

characterised by a relatively high value of "b", indicating that this variety of grape has a high yield of sugar. On the other hand a variety such as Gros Maroc has a low value of "b" for the final yield of sugar. On comparing the values of "b" for a given variety for the three seasons at Constantia it will be seen that they vary slightly, thus indicating a seasonal variation. In general, it will be seen that the longer growing period, as indicated by the lower values of "K", is associated with the larger ultimate sugar yield. It would appear that the more rapidly the products of the growth change appear, the sooner is the rate of change slowed down. At the same time it will be noticed that the variations in these two factors for the three seasons for Constantia grapes be within comparatively narrow limits. The mean values, therefore, may be regarded as being characteristic of the growth changes at Constantia and may well serve as a basis for comparison with the grapes from Paarl. On comparing the values of "b" for Paarl grapes with those for Constantia grapes it will be seen that the values are greater in the former case. The final yield of sugar at Paarl is higher, and from this point of view, it would seem that the conditions at Paarl are better adapted to the vine growing industry. At the same time it will be noticed that the difference is greater with an early ripening variety such as White Hanepoot and this would seem to show that the changes in the climatic conditions at Paarl during the 1927 season had a greater resultant effect upon the earlier ripening varieties. In accordance with the view that a high crop yield is associated with a long growing period, it will be noticed that the values of "K" for Paarl grapes are all very much smaller than the corresponding values for Constantia grapes. The conditions at Paarl tend to favour a longer effective growing period. The fact that "b" is the limiting value of the sugar content of the juice at Maturity under normal conditions of growth indicates that some factor must be present which tends to prevent an unlimited production of sugar. This result

would /

would be in accordance with the conception that the course of the growth change is influenced by a factor which is catalytic in character.

For the purpose of a more general comparison, however, the values of the growth velocity constant "k" and the growth capacity constant "b/K" may be compared. These expressions are calculated from the relationship K = kb and the figures obtained in this way are given in Table VI.

TABLE VI.

Locality.	Variety.	Year.	k	$\frac{b}{K} \times 10^{-2}$
Constantia.	White Hanepoot.	1925	0.00193	5.17
		1926	0.00180	5.69
	Red Hanepoot.	1923	0.00188	5.33
		1925	0.00196	5.09
		1926	0.00177	5.64
	Gros Maroc.	1925	0.00236	4.24
		1926	0.00265	3.77
	Barbarossa.	1923	0.00252	4.00
		1925	0.00250	4.00
		1926	0.00236	4.24
	Waltham Cross.	1925	0.00179	5.59
		1926	0.00180	5.60
	Flaming Tokai.	1923	0.00236	4.24
		1925	0.00249	4.02
		1926	0.00256	3.91
Paarl.	White Hanepoot.	1927	0.00105	9.46
	Barbarossa.	1927	0.00166	6.05
	Flaming Tokai.	1927	0.00166	6.02

On comparing the values for each variety it is clearly seen that those varieties with a low value of "k", i.e., those which are associated with a long growing period, are characterised by a high final yield of sugar. It will also be seen that for any particular variety the velocity constant

"k"/

"k" varies slightly in one locality according to the season. At the same time this variation lies within comparatively narrow limits. Subject to these reservations the value of "k" is apparently an inherent constant. Under unfavourable seasonal conditions the value of "k" tends to be low and the attainment of maturity is retarded. As has been pointed out by Kidd, West and Briggs[23] external conditions must directly affect the absolute value of the growth rate. The fact that the general form of the change remains the same during the different seasons is evidence of the conclusion that the production of sugar is conditioned by internal factors.

As a result of the theoretical basis upon which these results are founded it is to be expected that the constant "k" would vary in an inverse ratio to the final yield of sugar. In accordance with the fact that the final yield of sugar for Paarl grapes is greater than for Constantia grapes it is found that the value of "K" for Paarl grapes is distinctly less than for Constantia grapes. It is clear that "K" is affected by environmental factors. Since K = kb it would be expected that the value of the constant "k" would also show the same trend of variation; reference to Table VI indicates that such is the case. It can only be concluded that this factor is distinctly affected by conditions of environment. Such a result might be expected from the point of view of chemical dynamics since "k" is the velocity constant of the transformation. Gregory[20] points out that in plants the relative dry weight increase is not solely conditioned by external factors, but depends also on the action of varying internal factors. Even were the external factors to remain constant at their mean values the rate of a process such as relative dry weight increase would not remain constant at its mean value. The results, here obtained, bear out this view. The present results are in direct contradistinction to the views of Robertson who has based his arguments upon the similarity of the values of "k" obtained in the cases of British and Australian infants. It

can /

can only be concluded that the constancy of this factor in the cases he mentions is due to causes which do not operate in the case of plants. In the first place the evolution of the higher types of animals has been accompanied by an increasing perfection of the various mechanisms which are adapted to maintain constancy of the cell medium. This factor would endow the higher types of animals with a greater capacity for resisting changes in external conditions than is the case with plants. On the other hand it may be that with genetically related races the different constants are subject to variations whose limits are extremely narrow. The results, here obtained for grapes, permit of no doubt that the velocity constant "k" is definitely affected by external conditions, particularly in the case of environment. The explanation of Robertson's results must depend upon the existence of some mechanism in the case of animals which compensates the influence of environment, so that the magnitude of final growth is not closely related to the period of growth. In such a case a high final crop yield would not necessarily be associated with a long growing period. This view is shown to be incorrect when applied to the growth of plants. It would seem that Robertson has overlooked the significance to be attached to "k" in his argument. Gregory[20] has found in the case of barley that there is a positive and negative correlation with total radiation of net assimilation rate and relative leaf growth rate respectively and this provides a mechanism whereby the yield of the plant tends to remain within fairly narrow limits in spite of climatic variation. These conclusions are borne out in the present results. In the case of the Constantia grapes, where the samples were all obtained from one locality, the various constants lie within comparatively narrow limits indicating the relatively small effect of seasonal variations. Under such conditions there is no doubt that "k" has an inherent value which is characteristic for each variety. When, however, the environment is altered it would appear that the internal factors

are /

are directly affected since the growth constants assume entirely new values. "k," then, is a constant which has a specific value for different varieties of plants only <u>under comparable conditions of growth</u>.

As a final comparison between the different varieties the value of the growth capacity constant "b/K" may be considered. This is a characteristic which varies directly with the crop yield and therefore forms a direct means of comparison between different varieties under the same conditions or between the same variety under different conditions. The values obtained from the experimental data are given in Table VI. In the first place it will be noticed that rapid growth (as shown by a high value of "k") is associated with a low growth capacity constant. For example, the Hanepoots have a comparatively low value of "k" but are characterised by a relatively high growth capacity for sugar. On the other hand a variety, such as Flaming Tokai, ripens more or less rapidly, but the capacity for production of sugar is comparatively low. In practice, of course, the value of a variety is not necessarily completely measured by the magnitude of this constant. The value to be attached to the characteristic properties of any variety is dependent upon the requirements of the grower, since the flavour of the grapes is dependent upon other factors such as the relative proportions of acid and sugar in the ripe berry.

In the case of Paarl grapes it is seen that, in accordance with the variation in the growth velocity constant, the value of growth capacity constant is very much greater than for Constantia grapes. From the point of view of the comparison of the same variety of grape grown in different localities it can be seen that this constant has a definite significance as affording a direct means of comparison between the varieties. It would be valuable to have a series of controlled experiments in which some idea might be obtained of the value to be placed upon the influence of external factors, such as temperature, sunshine, soil conditions, etc., in so far as differences in the

growth /

growth capacity constant are concerned.

If the value of "k" be known, the rate at which the growth products are being formed can readily be determined. The rate of growth is initially slow but gradually increases to a maximum value which is reached at the "half period" stage. After this point the reverse series of changes sets in. These changes are clearly shown in Fig.2 where the daily rates, corresponding to the times of analyses, are plotted against the time in the case of the White Hanepoots from Paarl in 1927 and from Constantia in 1926 (the remaining varieties yield exactly similar forms of curves). It will be seen that the agreement between experiment and theory is good. The total time during which the full cycle of changes takes place corresponds to the "grand period of growth". In the figure the point of maximum rate of growth coincides with the "half period" of growth. On comparing the two curves it will be seen that the curve for Constantia grapes differs considerably from that for Paarl grapes. It indicates that the growth changes are more rapid at Constantia and are spread over a somewhat shorter period of time. That this difference is not merely due to seasonal variations may be seen by reference to Fig. 3 where the growth rates for Red Hanepoot have been plotted for the three seasons 1923, 1925 and 1926. In this case it will be seen that, for three different seasons, the curves are all very similar in form and that the profound difference, as shown in Fig.2 for the same variety of grape from two different localities is not evident. Apparently changes in environment have a greater effect upon the internal factors of growth than have climatic variations. As may be seen from Fig.3 the resultant effect of seasonal variations is to cause mainly an alteration in the times at which the successive changes take place. Thus, the "half period" is reached at a slightly later date in 1926 than in 1923 and 1925, indicating the retarding effect of an unfavourable season. (Similar results are obtained with the other varieties). The effect of temporary climatic variations is shown by the fluctuations of the rates about the mean values,

as /

as given by the theoretical curves. When the "rate curves" for all the varieties are compared for a given season the characteristic differences can then be clearly seen. In Fig.4 the curves for the 1926 season are given (this season is used since a more complete record for all six varieties was available). For the sake of clarity the theoretical curves only are shown. It will be seen that the six varieties can be grouped into two distinctive classes. The Hanepoots and Waltham Cross are early ripening varieties compared with Gros Maroc, Barbarossa and Flaming Tokai, the maximum growth rate being reached at an earlier period in the former varieties. The former are also characterised by a longer "grand period of growth" and, in accordance with the theoretical deductions are associated with a higher ultimate sugar yield. The Hanepoots are characterised by a higher growth rate at the "half period" than any of the remaining varieties.

"The grand period curve", however, as defined by Sachs is the curve of actual increment per unit of time plotted against time and not of growth rate. The type of curve obtained in this way, however, is of exactly the same form as the above, as may be seen by reference to Fig.5. The observed weekly increments of sugar indicate somewhat large variations in the growth of the berry, and these may be accounted for by the temporary fluctuations in the climatic conditions. This is particularly noticeable during the latter portion of the season. During the early part of this season the climate was more or less uniform, but later the climate was subject to much fluctuation. The deviations from the theoretical curve are clear evidence of these changes, and should show a close relationship with the climatic variations. If, however, the average increments were determined by taking the mean value for two weeks the temporary fluctuations become less and the two curves more nearly agree, as shown by the dotted line. The nature of the "grand period" curve tends to show that there is an absence of internal morphological changes in the berry during the process of ripening. Kidd, West and Briggs (23) have

found /

found that the subsidiary maxima and minima which are evident in the later portion of the growth rate curve for a whole plant such as maize are closely correlated with the appearance of the male and female flowers on the plant. These maxima and minima are therefore due to internal changes which do not take place in the fruit itself.

From a consideration of the curve for the "grand period of growth" it is clear that in the very early stages of development of the berry the amount of sugar must be very small, but that at a later stage the amount increases rapidly. It is justifiable to assume that the sugar only commences to be formed in appreciable quantities after the berry has reached a definite stage of development. This stage is, in fact, coincident with the stage known to the French as the "veraison". It seems that the growth of the berry may be divided into two cycles, namely, the period of initial growth and the ripening period. This point will be dealt with later in dealing with the changes in acidity in which these two periods are more clearly defined.

(b) SOLUBLE SOLIDS IN THE JUICE.

On attempting to apply the simple form of the Robertson equation to the changes which occur in the soluble solids in the juice, it was found that the agreement between the calculated and observed values was extremely poor. However, by means of a slight modification in the form of the equation an expression was obtained which was found to give a very close agreement with the experimental values. This change was effected by deducting an initial value from the readings so that the following modified expression was found to be suitable

$$\log \frac{x - c}{(d - c) - (x - c)} = K(t - t_1) \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where "c" is the initial value to be subtracted.

Equation (1) simplifies to

$$\log \frac{x - c}{d - x} = K(t - t_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

By differentiation

$$\frac{dx}{dt} = k(x - c)(d - x)$$

where /

where "k" is the specific velocity constant of the change. It follows that the rate of increase of soluble solids is autocatalytic in character and is proportional to (i) the amount of material formed in excess of some minimum value and to (ii) the deficiency from the final maximum yield. Fr[om] the equations it can readily be seen that $K = k(d - c)$ and that the growth rate reaches a maximum when $x = \frac{d + c}{2}$; at this stage $t = t_1$.

It is clear that this equation is only applicable to the observational data when "x" is greater than "c"; in other words the soluble solid content of the juice must have a value "c" before the changes represented by the above equation can take place. It follows then that this cycle of growth does not commence from zero concentration of soluble solids and that the changes prior to the onset of this growth cycle must culminate in a growth yield of "c" grams of soluble solids. When this stage has been reached another growth cycle, autocatalytic in character commences and during this latter cycle the soluble solid content of the juice increases from "c" grams to "d" grams per 100 c.c. The growth yield of the second cycle is therefore "(d - c)" with a final crop yield of "d" grams for the two cycles. Apparently during the initial growth cycle the main products are organic nitrogenous compounds and acids together with small quantities of sugar. The value of "c" therefore represents the amount of soluble solids at a stage when the sugar commences to be formed in appreciable amounts. Owing to the times at which the investigations were commenced in 1923, 1925 and 1926, no data are available for an examination of this initial period of growth. The possibility of the soluble solids commencing with zero value seems to be ruled out by the results obtained in 1927 for Paarl grapes. This point will be discussed later.

The experimental data have been expressed in terms of grams of soluble solids per 100 c.c. of juice and are given in Tables VII - X. The method of determination has already been given.

Table VII. /

TABLE VII.

Constantia Grapes pressed in 1923.

Date.	Red Hanepoot.	Barbarossa.	Flaming Tokai.
28. 1.23	13.20	-	-
7. 2.23	18.14	14.46	15.02
14. 2.23	17.04	13.27	16.00
21. 2.23	19.67	13.36	15.12
28. 2.23	20.38	17.22	17.22
7. 3.23	21.68	20.38	21.77
14. 3.23	22.46	17.20	20.36
21. 3.23	26.20	17.98	20.97
28. 3.23	27.42	19.52	22.49

TABLE VIII.

Constantia Grapes pressed in 1925.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28. 1.25	10.45	10.14	7.71	5.57	10.12	7.14
4. 2.25	11.78	13.08	10.00	10.38	11.00	11.36
11. 2.25	15.36	15.06	13.99	12.60	13.86	13.97
18. 2.25	16.80	17.55	13.36	13.33	16.48	16.28
25. 2.25	19.43	17.84	15.59	16.82	20.87	16.42
4. 3.25	20.13	21.02	19.25	17.66	17.24	19.40
11. 3.25	21.75	20.74	19.90	19.53	17.67	22.20

TABLE IX.

Constantia Grapes pressed in 1926.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
13. 1.26	4.90	5.16	5.37	4.74	8.16	4.63
20. 1.26	7.22	6.54	5.29	5.21	8.41	4.95
27. 1.26	11.03	10.67	5.76	5.02	10.54	6.93
3. 2.26	12.73	13.23	7.20	7.58	12.31	8.26
10. 2.26	13.15	14.13	9.77	11.79	15.30	10.40
17. 2.26	17.17	17.11	11.94	13.61	14.98	11.98
24. 2.26	19.00	19.38	15.18	15.96	16.59	15.60
3. 3.26	20.06	21.08	16.08	16.96	20.14	16.85
10. 3.26	24.01	21.59	17.40	18.34	-	18.10
17. 3.26	22.10	20.38	17.76	19.61	-	17.56
24. 3.26	24.40	23.06	17.86	-	-	19.30

TABLE X.

Paarl Grapes pressed in 1927.

Date.	White Hanepoot.	Barbarossa.	Flaming Tokai.
30.11.26	5.44	5.32	5.36
7.12.26	5.54	5.58	5.10
14.12.26	5.42	5.43	5.02
21.12.26	5.61	5.53	5.51
28.12.26	5.96	5.97	5.55
4. 1.27	7.42	6.05	5.54
11. 1.27	8.36	6.43	6.40
18. 1.27	10.49	7.06	9.78
25. 1.27	12.47	7.62	8.96
1. 2.27	14.56	8.95	12.44
8. 2.27	15.58	11.54	12.95
15. 2.27	18.46	16.33	15.86
22. 2.27	18.43	17.67	14.18
1. 3.27	22.69	19.71	16.33
8. 3.27	22.84	18.11	16.77
15. 3.27	23.40	19.57	18.26
22. 3.27	25.44	21.44	19.78
29. 3.27	25.65	21.68	20.18

It will be noticed that in the case of the results for 1927 the soluble solids show very little change during the first three or four weeks of the investigation. There does not seem to be any clear indication of an increase from a zero value.

The values for the constants as given in equation (2) for the soluble solids have been calculated from the experimental data for the different seasons and are given in Table XI. The time has been reckoned in days from the commencement of observation and logarithms to the base 10 were used.

Table XI. /

TABLE XI.

Soluble Solids – $\log \frac{x - c}{d - x} = K(t - t_1)$.

Locality.	Variety.	Year.	c	d	K	t_1
Constantia.	White Hanepoot.	1925	3.86	22.46	0.0380	8.0
		1926	3.85	24.50	0.0379	25.0
	Red Hanepoot.	1923	3.87	23.00	0.0360	2.0
		1925	3.90	22.10	0.0360	7.5
		1926	3.84	23.55	0.0362	26.5
	Gros Maroc.	1925	4.28	21.10	0.0413	15.0
		1926	3.95	18.35	0.0410	31.5
	Barbarossa.	1923	3.20	20.48	0.0410	9.0
		1925	3.80	20.20	0.0416	13.5
		1926	3.50	20.10	0.0414	31.0
	Waltham Cross.	1925	3.55	21.00	0.0352	9.0
		1926	3.70	21.20	0.0329	20.0
	Flaming Tokai.	1923	3.50	22.60	0.0410	9.0
		1925	4.62	22.75	0.0456	15.5
		1926	4.04	20.00	0.0396	33.5
Paarl.	White Hanepoot.	1927	4.75	26.82	0.0248	70.0
	Barbarossa.	1927	4.65	22.15	0.0313	74.0
	Flaming Tokai.	1927	4.80	21.05	0.0301	73.0

When the calculated values are plotted their agreement with the observed values is seen to be close (see Fig.6) The results for 1926 are given as embodying the greatest number of varieties. On account of the time at which the observations were commenced in 1923 and 1925 the initial lag in the curve is not evident but the results have been calculated on the assumption that the type of change found suitable for the 1926 and 1927 seasons is equally suitable for the remaining seasons. The similarity of the change during this particular cycle for the soluble solids with that for the sugars is clearly seen.

From Table XI it will be seen that the value of "c" for grapes grown at Constantia is approximately 4.0 per cent. but that the value for corresponding varieties at Paarl is

slightly /

slightly greater so that the commencement of this second cycle of growth at Paarl is characterised by a slightly higher initial concentration of soluble solids in the juice. As already mentioned, it will be noticed that the changes in the soluble solids for the first three or four weeks of the investigation of grapes grown at Paarl are very small, practically negligible. The investigation in this season was commenced at an early date, which, judging from other sources of information, was about two to three weeks after the appearance of the berries on the bunch. It would therefore appear that "c" must practically be the concentration of soluble solids at the stage when the berry is initially formed. It is found that, following the initial formation of the berry, the acid in the juice increases in amount. The consequent increasing amount of soluble solids must therefore be masked by some secondary change. In reality it is only when the sugar commences to be formed in appreciable quantities that the changes in the soluble solids show any apparent increase. In a paper on "Growth and Sap Concentration" Reed[(32)] has shown that a high sap concentration is associated with the slower growth of a shoot and fruit-bud formation. The above changes may, therefore, find a possible explanation in the changes occurring in the sap of the bunch during the growth of the berry. In the initial stages of growth of the berry the principal constituents forming the soluble solids consist of acids together with small quantities of nitrogenous organic compounds, mineral constituents and traces of carbohydrates.

In the expression, "d" has the same significance as "b" in the case of the sugars. It represents the maximum yield of soluble solids in the berry under normal conditions of growth. At the same time it must be remembered that it represents, in this case, the growth yield as the resultant of of two growth cycles. The actual crop yield of the second cycle is represented by "d - c". Since $K = (d - c)k$, the value "k", the growth velocity constant of the second cycle, may be

readily /

readily obtained from the experimental data. The values of "K", "k", and "d" will be subject to variations in accordance with changes in the external conditions to the same extent as in the case of the sugar content of the juice, and may be expected to vary in the same way. In the present case the growth capacity constant, as calculated from the expression "$\frac{d - c}{K}$" represents the constant for the second cycle of growth. It is therefore an index of the yield for the second cycle.

In the expression as adopted $t = t_1$ when $x = \frac{d + c}{2}$ i.e. $x = \frac{d - c}{2} + c$. From this, it follows that "t_1" is the half period of the change from a concentration "c" to the final concentration "d". In the present work, as in the case of the sugar, the value of "t_1" is only comparable for the different varieties during a given season owing to the variations in the times at which the work was commenced during the different seasons. On comparison of the different values obtained it will be seen that exactly the same division between the different varieties can be made as in the case of the "half period" for the changes in the sugar content. The same differences between the values of "t_1" for early- and late-ripening varieties is clear. On comparing the values of "t_1" for the soluble solids with the corresponding values for the sugars it will be seen that there is very little difference in the values. In some cases there seems to be a very slight lag in the rate of change of the soluble solids behind the change in the sugar content of the juice. If the grand period of growth be taken into account it would be seen that the time of growth for the second cycle is approximately the same as the period of growth for the total change of sugar content. The same retardation in the attainment of the "half period", according to season, is evident. These facts indicate that there is a very close relationship between the sugar and soluble solid content of the juice. This point will be dealt with later. On comparing the growth rate curves for the sugar and soluble solids in the juice it would be seen that, during the initial

period /

period of increasing growth rate, the soluble solids have a slightly lower growth rate than the sugar. This is apparently mainly due to the fact that the acid is decreasing rapidly during this stage. When the rate of decrease of acid becomes slow the rate of change of both the sugar and the soluble solids becomes practically identical.

From Table XI it can be seen that the final yield of soluble solids, as given by "d", varies for different varieties in different seasons in the same way as in the case of the final yield for the sugar content. In the case of the varieties from Paarl, the value of "d" is greater for White Hanepoot and Barbarossa than at Constantia, but the value is approximately the same in the case of Flaming Tokai. This result may possibly be due to the fact that the latter variety is a late-ripening grape and that the change in the climatic conditions in 1927 brought about an acceleration in the ripening processes with the consequent tendency towards a lowering of the crop yield. The value of the concentration of the soluble solids at maturity differs from the value of the sugar concentration by approximately 2 per cent., and therefore, at maturity, it appears that about 90 per cent. of the soluble solids in the juice consists of sugar. When the values of "d" are taken in conjunction with the values of "K" it will be seen that a high crop yield is associated with a low value of "K" and that the latter value is affected by seasonal conditions. In every case the values of "K" for Paarl grapes are distinctly lower than the corresponding values for Constantia grapes. This is in complete accordance with the results obtained for the changes in the sugar content. It is clear that changes in environment affect this constant more profoundly than do seasonal variations and the lower values for Paarl grapes indicate a longer effective growing period with the consequent fuller development of the fruit.

If the values of the growth velocity constant "k" as given in Table XII be compared, it will be seen that for a

given /

given locality this constant varies for each variety according to the season, but the variations lie within comparatively narrow limits. With these reservations, therefore, the value of "k" has an inherent value characteristic of each variety. When the values for the corresponding varieties at Paarl and Constantia are compared it will be seen that the change in environment brings about a very much greater change in the value than does any seasonal variation. The values of "k" for Paarl grapes are very much lower than for Constantia grapes. As in the case of the changes in the sugar content of the juice, it may be concluded that the internal factors governing the production of soluble solids are more influenced by changes in locality than by seasonal changes.

TABLE XII.

Locality.	Variety.	Year.	$k = \frac{K}{d - c}$	$\frac{d - c}{K} \times 10^{-2}$
Constantia.	White Hanepoot.	1925	0.00204	4.90
		1926	0.00188	5.32
	Red Hanepoot.	1923	0.00188	5.32
		1925	0.00198	5.05
		1926	0.00184	5.44
	Gros Maroc.	1925	0.00246	4.07
		1926	0.00285	3.51
	Barbarossa.	1923	0.00237	4.22
		1925	0.00254	3.94
		1926	0.00249	4.02
	Waltham Cross.	1925	0.00202	4.95
		1926	0.00190	5.26
	Flaming Tokai.	1923	0.00215	4.65
		1925	0.00251	3.98
		1926	0.00250	4.00
Paarl.	White Hanepoot.	1927	0.00112	9.00
	Barbarossa.	1927	0.00180	5.60
	Flaming Tokai.	1927	0.00186	5.40

It will be seen that the value of "k" in this case

is /

is very nearly the same as the corresponding value for the changes in the sugar content of the juice. It seems clear that the major portion of the changes which take place in the juice of the berry during the ripening period must be due almost entirely to the changes which take place in the sugar content. These latter are so great as to impress their character upon the whole course of change during the ripening period.

As a more suitable means of comparison between the varieties during this second cycle of growth the values of the growth capacity constant, as given in Table XII, may be taken. These values show clearly that a high value for the growth capacity is associated with a long growing period, i.e., with a low value of "K" or "k". The value is practically the same as the corresponding value for the sugar and, therefore, the order in which the varieties may be placed according to the magnitude of this constant is the same. The effects of seasonal conditions are evident in the variations of this constant when the values for a given variety in one locality are compared. The more evident effect of change in environment is clear when the corresponding values for Paarl and Constantia grapes are compared. It will be seen that the greatest effect has been in the case of White Hanepoot where the growth capacity constant has increased at Paarl by nearly 80 per cent. of its value at Constantia. It is again clear that this constant offers a convenient method of direct comparison between different varieties under the same conditions or between the same variety under different conditions.

On comparing the values of the constant "K" for the growth changes in sugar, soluble solids and the value of "k" for the acid (see later), it was found that the constant for the soluble solids was practically the weighted mean of the constants for the sugar and acid. In other words, the change in the soluble solids is almost entirely due to the sum of the changes which take place in the sugar and acid content of the juice.

It /

It was found that

$$K_2(s + a) = K_1 s + ka$$

where "K_1", "k" and "K_2" are the constants for the sugar, acid and soluble solids respectively and "s" and "a" are the final growth yields of sugar and acid (the acid, of course, decreases during ripening while the sugar increases). The values for K_2 observed and calculated are given in Table XIII.

TABLE XIII.

Locality.	Variety.	Year.	K_2(obs.)	$K_2 = \frac{K_1 s + ka}{s + a}$
Constantia.	White Hanepoot.	1925	0.0380	0.0380
		1926	0.0379	0.0375
	Red Hanepoot.	1923	0.0360	0.0376
		1925	0.0360	0.0374
		1926	0.0362	0.0364
	Gros Maroc.	1925	0.0413	0.0415
		1926	0.0410	0.0403
	Barbarossa.	1923	0.0410	0.0405
		1925	0.0416	0.0430
		1926	0.0414	0.0410
	Waltham Cross.	1925	0.0352	0.0344
		1926	0.0329	0.0332
	Flaming Tokai.	1923	0.0410	0.0445
		1925	0.0456	0.0450
		1926	0.0396	0.0407
Paarl.	White Hanepoot.	1927	0.0248	0.0249
	Barbarossa.	1927	0.0313	0.0305
	Flaming Tokai.	1927	0.0301	0.0297

It may therefore be concluded that the changes which take place in the juice during ripening are almost entirely those due to the sugar and acid and that the changes in the other constituents have little effect upon the ultimate quantitative growth yield. The effect of these constituents may, of course, be important in regulating the course of the changes. As a

matter /

matter of fact the first conclusion agrees with the data which have been obtained and is in agreement with the conclusions of other workers. In this connection Bioletti, Cruess and Davi[5] find that the cream of tartar showed very little increase during ripening; in most cases the final amount of cream of tartar was less than 0.80 grams per 100 c.c. Frater [17] found that the average ash content of 44 varieties of ripe wine grapes was only 0.23 per cent.. Lewis [26] states that the ash content increases on an average by about 50 per cent. during ripening. Since it has been found [26] that at maturity the ash content of the juice was only about 0.30 per cent., the whole increase could have very little effect upon the quantitative yield of soluble solids in the berry. In a previous paper it has been shown [12] that in 1925 the change in the total ash of the berry was on an average from 0.25 per cent. to 0.50 per cent. At the same time, the protein content of the juice was found to vary irregularly, any increase being very small, and the total protein content of the juice was about 0.20 per cent. In these circumstances, then, it is clear that the conclusions regarding the changes in the soluble solids must be justifiable.

In the later stages of ripening in the grape the amount of acid becomes relatively small in comparison with the amount of sugar and the rates of production of sugar and soluble solids become practically identical. In the expression $K_2(s + a) = K_1 s + ka$, the value of "ka" is small. Under these circumstances, therefore, it may be expected that the relationship between the sugar and soluble solids would be very close and, in fact, tend to be linear. Bioletti, Cruess and Davi[5] draw attention to the fact that the differences between these two factors become less as the grapes ripen but they have drawn no general conclusions regarding this fact. It has been found that the Balling (or Brix) degrees of the juice gives, within the limits of experimental error, the amount of soluble solids per <u>100 grams of juice</u>. At maturity it has been shown[13] that there is a general difference of 0.8 - 1.2 between the Balling

degrees /

degrees of the juice and the sugar content per 100 c.c. Thus, by subtraction, a close approximation may be obtained to the sugar content of the juice at maturity.

The Balling hydrometer only gives a direct estimation of the sugar content when no other interfering substances are present. Caldwell[9] has drawn attention to the difficulties of using specific gravity determinations in calculating the sugar content of fruit juices and it is pointed out that accurate analyses of each type of fruit juice is necessary before a spindle can be used with any degree of accuracy for this purpose. When the conclusions regarding the changes in the sugar and soluble solid content of the juice are taken into account it is possible to obtain an accurate estimate of the sugar content of grape juice from the Balling reading of the juice.

The changes in the sugar content of the juice have been shown to be represented by the equation

$$\log \frac{y}{b - y} = K_1(t - t_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where "y" is the sugar content at time "t", "b" is the amount of sugar at maturity, "K_1" is a constant and $t = t_1$ when $y = b/2$.

The changes in the soluble solid content of the juice are expressed by the equation

$$\log \frac{x - c}{d - x} = K_2(t - t_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where "x" is the soluble solid content at time "t"; "$d - c$" is the change of soluble solid content during this cycle; "K_2" is a constant and $t = t_2$ when $x = \frac{b + c}{2}$.

Eliminating t from these two expressions the following expression is obtained to express the sugar in terms of the soluble solids

$$K_2 \log \frac{y}{b - y} - K_1 \log \frac{x - c}{d - x} = K_1K_2(t_1 - t_2)$$

It has been shown that "K_1" is very nearly equal to "K_2" since the changes in the acid content of the juice are small compared with the changes in sugar content. The "half periods" "t_1" and "t_2" are practically coincident. As a first approximation the expression therefore reduces to

$$\frac{y}{b - y} = \frac{x - c}{d - x}$$

On /

On simplification this becomes

$$y = \frac{b}{d - c}(x - c) \quad \text{or} \quad y = m(x - c)$$

It has been shown that the values of "b", "d" and "c" vary for each type of grape and therefore the value of "m" may be expected to show variations for each type of grape. Since, however, the constants for any given variety in one locality vary within comparatively narrow limits with the seasonal conditions, the expression for any one variety will be generally applicable in the case of this variety for any season. This has been found to be the case and in Table XIV the values of "m" and "c", calculated from "b", "d" and "c" for each variety at Constantia are given

TABLE XIV.

Variety.	m	c
Hanepoot.	1.08	3.86
Gros Maroc.	1.11	4.12
Barbarossa.	1.08	3.50
Waltham Cross.	1.13	3.63
Flaming Tokai.	1.04	4.05

As was pointed out in the introduction, the White and Red Hanepoots may be regarded as identical so far as their characteristic properties are concerned. The constants for "Hanepoot" therefore are the average for both varieties. The very close agreement between the observed and calculated readings is shown in Fig.7A in which the values for the Hanepoots for 1923, 1925 and 1926 are included. It is clear that the assumption upon which the results are based must be justifiable. The equation so developed represents closely the true conditions. In the case of grapes it is clear that the amount of soluble solids is directly dependent upon the amount of sugar in the juice, If the soluble solids had been expressed in the form of x_1 grams per 100 grams of juice, then the amount of sugar per 100 c.c. would be given by the expression

$$y = m(x_1 d - c)$$

where /

where "d" is the density of the juice.

In practice it has been found that "x_1" is equal to the Balling degrees of the juice so that the amount of sugar per 100 c.c. will be given by

$$y = m(Bd - c)$$

where "B" is the Balling degrees of the juice. The corrections for temperature variations can be readily applied with the aid of tables. The method adopted in determining the Balling degrees of the juice has already been mentioned. The results obtained are given in Tables XV - XVIII in which the Balling reading has been corrected to 20°C.

TABLE XV.

Constantia Grapes pressed in 1923.

Date.	White Hanepoot.	Red Hanepoot.	Barbarossa.	Flaming Tokai.
31. 1.23	-	12.0	-	-
7. 2.23	15.7	16.6	14.0	14.1
14. 2.23	16.1	15.8	12.3	15.6
21. 2.23	16.6	17.8	12.8	14.6
1. 3.23	18.1	18.3	16.0	15.8
7. 3.23	18.2	20.1	19.1	19.9
14. 3.23	20.9	20.4	16.8	19.0
21. 3.23	23.7	23.5	16.3	18.7
28. 3.23	24.2	23.9	17.9	20.1

TABLE XVI.

Constantia Grapes pressed in 1925.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28. 1.25	10.5	9.8	7.9	5.9	10.1	7.4
4. 2.25	11.6	12.9	10.2	10.3	11.1	11.4
11. 2.25	15.0	14.8	13.7	12.5	13.6	13.8
18. 2.25	16.1	16.9	13.1	13.2	16.1	15.8
25. 2.25	18.5	17.0	15.1	16.1	19.7	15.7
4. 3.25	19.1	19.9	18.4	16.9	16.7	18.4
11. 3.25	20.5	19.7	18.9	18.4	16.9	20.9

Table XVII /

TABLE XVII.

Constantia Grapes pressed in 1926.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
13. 1.26	4.8	5.1	5.3	4.7	7.9	4.6
20. 1.26	7.0	6.4	5.2	5.3	8.2	4.9
27. 1.26	10.5	10.0	5.7	5.0	10.1	6.8
3. 2.26	12.2	12.6	7.0	7.4	11.8	8.0
10. 2.26	12.7	13.9	9.4	11.6	14.8	10.4
17. 2.26	16.4	16.2	11.9	12.8	14.6	12.1
24. 2.26	17.7	18.0	14.4	15.3	15.6	15.1
3. 3.26	19.0	20.1	15.7	16.3	19.0	16.3
10. 3.26	22.0	20.3	16.8	17.6	-	17.3
17. 3.26	20.8	19.1	17.3	18.5	-	17.1
24. 3.26	22.3	21.6	17.3	-	-	18.3

TABLE XVIII.

Paarl Grapes pressed in 1927.

Date.	White Hanepoot.	Barbarossa.	Flaming Tokai.
7.12.26	5.8	6.1	5.7
14.12.26	5.4	5.5	5.4
21.12.26	5.5	5.4	5.5
28.12.26	5.9	5.8	5.5
4. 1.27	7.5	6.1	5.5
11. 1.27	8.0	6.0	6.1
18. 1.27	9.5	6.7	9.3
25. 1.27	11.6	7.3	8.5
1. 2.27	13.6	8.5	11.8
8. 2.27	14.8	11.0	12.3
15. 2.27	16.9	15.4	14.6
22. 2.27	17.8	16.9	13.5
1. 3.27	20.8	19.4	15.1
8. 3.27	21.3	17.0	15.9
15. 3.27	21.6	18.0	17.1
22. 3.27	22.7	19.6	18.3
29. 3.27	22.9	19.9	18.6

At /

At $20^{o}C$ a very close approximation to the amount of soluble solids per 100 c.c. of the juice can be obtained by means of the formula

$$\text{Soluble solids per 100 c.c.} = B + 0.0042B^2$$

In carrying out the determination the juice must be allowed to stand so that the suspended solids may settle out. If the correction for temperature be applied accurate results can be obtained. Under these conditions the amount of sugar per 100 c.c. of juice, to a very close approximation, will be given by the formula

$$y = m(B + 0.0042B^2 - c)$$

The expression in this form was the one used to determine the calculated values in Fig.7 and it will be seen how closely the values agree with the observed data. From Table XIV it will be seen that the deviations of "m" and "c" for the different varieties are not unduly large and it would seem that for a given locality a generalised expression would be accurate enough for practical purposes. In the case of grapes from Constantia such an expression would be

$$y = 1.09(B + 0.0042B^2 - 3.83)$$

The constants given in this expression were those employed in determining the calculated values in Fig.7A. Since it has been shown that the various constants are directly affected by environment, it would seem that different constants would be necessary if the expression were to be applicable in the case of grapes from a different locality. In table XIX the values of "m" and "c" for grapes from Paarl are given

TABLE XIX.

Variety.	m	c
White Hanepoot.	1.11	4.75
Barbarossa.	1.11	4.65
Flaming Tokai.	1.12	4.75

It will be seen that "m" is slightly greater than the value already obtained and this is apparently connected with the fact that the initial concentration "c" of soluble

solids /

solids has a somewhat higher value at Paarl than at Constantia. It is therefore apparent that environmental factors play a more dominant part in influencing the composition of a fruit than do seasonal conditions. The use of a particular formula would therefore seem to be dependent more upon the locality than upon the variety of grape. The generalised formula for Paarl grapes would be

$$y = 1.11(B + 0.0042B^2 - 4.72)$$

The agreement between the observed and calculated values is shown in Fig.7B. The differences between the two general formulae are not very large and in practice results of sufficient accuracy would readily be obtained by the use of a formula embodying the average values of the constants. In the present case such a formula would be

$$y = 1.10(B + 0.0042B^2 - 4.20)$$

The agreement between the observed and calculated values, using this formula is shown by dotted lines in Fig. 7A and 7B. As the values increase the discrepancy due to the differences in the initial composition of the juice tend to become less. It is clear that for practical purposes the changes in the sugar content of grape juice may be followed by means of the simple Balling reading provided that the precautions, as mentioned, be taken.

From the form of the expression $y = m(x - c)$ it follows that, when the soluble solids have a concentration of "c" grams per 100 c.c., the amount of sugar present must be zero or, at least, practically negligible. In practice, of course, there may be very small quantities of sugar present in the juice of the berry, even in the very early stages of growth. Priestley and Wormall[31] have shown that the reducing sugars in the sap of the vine have a concentration of 0.03 grams per 100 c.c. so that it seems unlikely that the concentration of sugar in the berry would ever be absolutely zero.

(c) /

(c) ACIDITY OF THE JUICE.

In the 1926 and 1927 seasons the work was commenced at a much earlier stage than in the seasons of 1923 and 1925, and the data obtained showed that there are at least two well defined stages in the development of the acidity in grape juice. During the first stage (or initial growing period) the amount of acid in the juice increases to a maximum value. In the earlier seasons the work was commenced when this stage had already been passed. This stage has, however, been mentioned by other workers, such as Bioletti, Cruess and Davi[5] who state that the acidity increases owing to an increase of free acid. In the second stage the acidity showed a continuous decrease whose rate became less as maturity was reached. Lewis[26] has shown that the period of maximum acidity coincides with the beginning of the second period (or ripening period). It is clear that two processes at least are involved in the full growth cycle; first a period of production of acid and second a period of decrease. Unfortunately, sufficient data were only collected in 1927 to elucidate in any way the type of growth change occurring during the first period. This point will be dealt with later.

The most suitable expression to represent the changes in the acidity of the juice during the second or ripening period has been found to be given by

$$\log \frac{a}{x - a} = k(t - t_1)$$

In this expression "a" represents the final value of the acidity at maturity, "t" is the time when the acidity has a value "x" and "t_1" is the time reckoned from the commencement of observation or, when convenient, from the commencement of the decrease in acidity and is the period at which the acidity reaches a value of "2a". "k" is the velocity constant of the change.

From the point of view of the dynamics of chemical change it would be expected that "k" would be subject to variations according to the conditions of growth. Therefore /

Therefore external factors, such as temperature, rainfall, soil conditions, etc., may be expected to influence the value of "k". Seasonal variations and environmental changes should therefore be evident in the results.

Expression (1) may be written in the form

$$x = a(1 + e^{-k\overline{t - t_1}})$$

in which form it may be compared with the simple logarithmic function which had previously been adopted, namely, $x = ce^{-bt}$ (14) It will be seen that the first expression only differs from the original form by the addition of another factor. This factor, however, indicates that there is a definite limit to the decrease in acidity and that under the normal conditions of growth, the acid can not entirely disappear from the grape.

The rate of decrease of acidity is given by

$$\frac{dx}{dt} = -k(x - a)$$

During the period of ripening therefore the rate of decrease of acidity is proportional to the excess of acidity over the minimum value at maturity. As the acidity decreases the excess of acidity becomes less with the consequent decrease in the rate of change. Ultimately, at maturity, the excess concentration of acid becomes very small and the rate of change is practically negligible.

The experimental data obtained during the different periods of investigation are given in Tables XX - XXIII in which the acidity is expressed in terms of grams of tartaric acid per 100 c.c. of juice.

TABLE XX.

Constantia Grapes pressed in 1923.

Date.	White Hanepoot.	Red Hanepoot.	Barbarossa.	Flaming Tokai.
31. 1.23	-	1.99	-	-
7. 2.23	1.44	0.99	1.25	1.56
14. 2.23	1.14	1.06	1.24	1.29
21. 2.23	0.85	0.88	0.93	1.29
28. 2.23	0.76	0.68	0.78	0.92
7. 3.23	0.68	0.54	0.66	0.70
14. 3.23	0.56	0.54	0.61	0.62
21.3. 23	0.49	0.45	0.47	0.60
28. 3.23	0.52	0.44	0.45	0.44

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TABLE XXI.

Constantia Grapes pressed in 1925.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28. 1.25	2.81	3.10	3.72	3.31	2.04	4.02
4. 2.25	1.93	1.91	2.65	2.25	1.61	2.88
11. 2.25	1.45	1.45	1.71	1.84	1.11	1.69
18. 2.25	1.20	1.13	1.67	1.53	0.83	1.25
25. 2.25	0.76	0.84	1.25	0.81	0.64	0.96
4. 3.25	0.73	0.70	0.91	0.67	0.70	0.77
11. 3.25	0.68	0.67	0.90	0.67	0.62	0.70

TABLE XXII.

Constantia Grapes pressed in 1926.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
13. 1.26	3.25	3.30	3.67	2.97	2.82	3.40
20. 1.26	3.25	3.34	3.65	3.06	2.53	3.58
27. 1.26	2.25	2.46	3.64	3.12	2.02	3.54
3. 2.26	1.90	1.81	3.56	2.75	1.49	3.42
10. 2.26	1.61	1.70	2.81	1.92	1.25	2.67
17. 2.26	1.01	1.10	2.29	1.54	1.21	2.07
24. 2.26	0.89	1.01	1.69	1.20	0.98	1.46
3. 3.26	0.77	0.73	1.57	1.09	0.82	1.15
10. 3.26	0.70	0.72	1.14	0.96	0.72	0.98
17. 3.26	0.64	0.64	1.12	0.90	-	0.85
24. 3.26	0.60	0.54	1.02	-	-	0.80

Table XXIII /

TABLE XXIII.

Paarl Grapes pressed in 1927.

Date.	White Hanepoot.	Barbarossa.	Flaming Tokai.
30.11.26	2.68	2.22	2.22
7.12.26	2.97	2.30	2.50
14.12.26	2.96	2.40	2.70
21.12.26	3.20	2.62	3.06
28.12.26	3.38	2.80	3.10
4. 1.27	3.46	2.94	3.25
11. 1.27	3.23	2.87	3.32
18. 1.27	2.72	2.94	2.83
25. 1.27	1.74	2.65	2.09
1. 2.27	1.16	2.20	1.30
8. 2.27	0.84	1.55	0.98
15. 2.27	0.67	0.66	0.65
22. 2.27	0.61	0.57	0.64
1. 3.27	0.48	0.49	0.50
8. 3.27	0.50	0.46	0.48
15. 3.27	0.48	0.42	0.44
22. 3.27	0.43	0.40	0.36
29. 3.27	0.45	0.40	0.38

The initial increase in acidity can be clearly seen in Tables XXII and XXIII. The changes in Table XXIII up to the stage indicated by the dotted line will be treated later. The values for the constants given in Expression (1) calculated from the experimental data are given in Table XXIV. In the table "t_1" has been reckoned in days from the commencement of observation in seasons 1923 and 1925 and logarithms to the base 10 have been used. In the case of the results for 1926 and 1927 the figures given in the brackets indicate the time reckoned from the point at which the acid commences to decrease (i.e., from the point marked A_1 ... A_6 in Fig.8), the other figures are from the commencement of observation.

Table XXIV/

TABLE XXIV.

Acidity – $\log \frac{a}{x - a} = k(t - t_1)$.

Locality.	Variety.	Year.	a	k.	t_1	
Constantia.	White Hanepoot.	1923	0.42	0.0234	22.5	
		1925	0.40	0.0238	25.0	
		1926	0.45	0.0217	43.5	(36.5)
	Red Hanepoot.	1923	0.36	0.0267	26.0	
		1925	0.44	0.0275	28.5	
		1926	0.34	0.0193	56.5	(48.0)
	Gros Maroc.	1925	0.54	0.0243	31.5	
		1926	0.64	0.0185	57.0	(36.0)
	Barbarossa.	1923	0.45	0.0318	21.0	
		1925	0.43	0.0288	29.0	
		1926	0.56	0.0243	47.0	(27.5)
	Waltham Cross.	1925	0.48	0.0257	18.5	
		1926	0.54	0.0202	35.0	(30.0)
	Flaming Tokai.	1923	0.48	0.0309	26.5	
		1925	0.40	0.0292	33.5	
		1926	0.59	0.0242	51.5	(29.0)
Paarl.	White Hanepoot.	1927	0.40	0.0302	73.5	(28.0)
	Barbarossa.	1927	0.40	0.0348	79.0	(23.0)
	Flaming Tokai.	1927	0.36	0.0308	77.0	(30.0)

When these expressions are plotted in the form of curves it is seen that the agreement between the observed and calculated figures is very close. For the sake of clarity the curves have been given only in the case of the results for the 1926 season (see Fig.8). The agreement is equally good for the other seasons.

On account of the variations in the times of commencing the investigation in each of the different seasons, the values of "t_1" are generally only comparable for the different varieties in any one season. Thus, in the 1923 season, the value of "t_1" in days (i.e. the interval between the commencement of the work and the period when the acidity has a value "2a") varies

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in the following way :- 22.5, 26.0, 21.0, 26.5 days for White Hanepoot, Red Hanepoot, Barbarossa and Flaming Tokai respectively. This period may conveniently be termed the "half period". In the 1925 season the same interval was 25.0, 28.5, 31.5, 29.0, 18.5 and 33.5 days for White Hanepoot, Red Hanepoot, Gros Maroc, Barbarossa, Waltham Cross and Flaming Tokai respectively. These figures show clearly that Waltham Cross is an early ripening variety while Flaming Tokai and Gros Maroc are late ripening varieties. The remaining varieties occupy an intermediate position. On examining the results for the 1926 and 1927 seasons it will be seen that the initial period of increasing acid is clearly defined. After a maximum value has been reached the actual ripening period commences and the acid commences to decrease. In Fig. 8 this point has been marked on the curves by A_1 ----- A_6. At this point the initial curve of growth intersects the curve of the ripening period. From the commencement of observation this point is reached in about 7.0, 8.5, 21.0, 19.5, 5.0 and 22.5 days for the six varieties in the order already given. These figures clearly show that Waltham Cross commences to ripen earlier than any of the remaining varieties. It is closely followed, however, by the two Hanepoot varieties, while the remaining varieties begin to ripen much later and in the following order Barbarossa, Gros Maroc and Flaming Tokai. The length of time from the stage A taken to reach the "half period" varies as follows :- 36.5, 48.0, 36.0, 27.5, 30.0, 29.0 days in the order as above. These facts indicate that, although the Hanepoots begin to ripen at an early stage, they are a slow ripening variety and it would appear that these circumstances enable a greater development to occur so that the ultimate acid content of the juice of such a variety is low. In practice, of course, the point A will not be sharply defined. The curve will show a more gradual change at the stage where the changes of the initial growth period and those of the ripening period begin to fuse into each other. In the results for the 1927 season, the stage A was reached in about 45.5, 56.0, 47.0 days

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from the beginning of the investigation for White Hanepoot, Barbarossa and Flaming Tokai. The time taken from the point A to reach the "half period" was 28.0, 23.0 and 30.0 days for the same varieties. From these last figures it will be seen that in White Hanepoot and Barbarossa the acid decreases more rapidly during the ripening period at Paarl than at Constantia. This time, in the case of Flaming Tokai, seems to have been little affected. This would seem to be connected with the fact that this variety ripens later than the others.

In the equation "a" represents the minimum value of the acidity in the juice at maturity and, on comparing the values given in Table XXIV, it will be seen that the value varies slightly according to the variety of grape. For example, the mean value of the acidity for Constantia grapes at maturity is 0.42, 0.38, 0.60, 0.48, 0.50 and 0.50 per cent. for White Hanepoot, Red Hanepoot, Gros Maroc, Barbarossa, Waltham Cross and Flaming Tokai respectively. Thus, varieties, such as the Hanepoots which have a mild sweet flavour, are characterised by a low value of "a" while those, such as Gros Maroc with a somewhat tart flavour, have a relatively high value of "a". On the other hand the value of "a" does not seem to be subject to any very great variations due to seasonal conditions. In an unfavourable season the value tends to be slightly higher than in a favourable season, indicating a slightly more acid product at maturity. In the case of the Paarl grapes the minimum acidity was found to be 0.40, 0.40 and 0.36 per cent. for White Hanepoot, Barbarossa and Flaming Tokai respectively It will be seen that these values are slightly lower than in the case of the same grapes grown at Constantia. This indicates that the tendency is for the conditions at Paarl to be slightly more favourable to a greater degree of ripening. The differences found for each variety are 0.02, 0.08 and 0.14 in the same order as above. In the early part of the 1927 season the climatic conditions were unsuitable for the development of the grape and apparently the change in the weather occurred in sufficient time to allow a greater reduction in acidity to take place in the two latter

varieties /

varieties which ripen later than White Hanepoot. The fact that a limiting factor is obtained during the normal process of ripening indicates that the changes in acidity are subject to some controlling factor. Kidd, West & Briggs [24] show that there is a continuous falling off of respiration with increasing age and that the ratio of relative growth rate to respiratory index remains fairly constant throughout the life cycle.

When the values of "k", the velocity constant of the change, are examined, it will be seen that the variations in this constant are much more significant. In favourable seasons the value of "k" is greater than in unfavourable seasons and such a result is in accordance with the theoretical deductions. In 1926 the value of "k" is lower than in the remaining two seasons at Constantia. This variation is not confined to any one variety of grape but is the same in all cases. It thus appears that seasonal conditions have a direct effect upon the rate of change of the acid, but, as has been pointed out, the effect upon the magnitude of the acidity at maturity is relatively small. It may therefore be concluded that unfavourable seasons cause a retardation of growth and a delay in the attainment of maturity, even although there seems to be but little effect upon the final composition of the juice at maturity - at any rate, in grapes from one locality.

In the case of grapes grown at Paarl the value of "k" is found to be distinctly greater and evidently the decrease of acid takes place far more rapidly in this locality than at Constantia. It will be seen that for any variety the values of "k" for three widely differing seasons at Constantia do not deviate greatly from the mean value which, therefore, affords a convenient figure for comparison. It is clear from the results that the variations in the value of "k" are greater in the case of a different locality than for different seasons. The constant "k" would seem to be characteristic of the internal factors of the plant, but there is no indication of how far this is affected by any particular external factor such as temperature. In this connection the paper by Caldwell [9]

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is of interest. This author concludes that the variation in the composition of the juice of grapes is narrower under constant cultural conditions in one locality than in samples grown over a wide area under different cultural conditions. These conclusions are fully corroborated by the results here obtained. If the grapes are compared at the same stage of maturity in one locality it seems that the variations in acidity are even less than hitherto suspected. If the comparison be made with samples chosen at arbitrary periods in different seasons the differences in composition will naturally be large.

On examining the values of "k" in Table XXIV, it would appear that those varieties with a longer ripening period, i.e., with a low value of "k", are associated with a low acidity at maturity, e.g., the Hanepoots. Varieties such as Flaming Tokai have a relatively short ripening period but, in general, have a higher acidity at maturity. A low rate of ripening is thus associated with a low value for the acidity at maturity. From this point of view the values of the velocity constant should serve a useful purpose in crop studies.

Bioletti, Cruess and Davi[5] find that during ripening the total and free acid rapidly decrease. The increase in cream of tartar is very slow but usually fairly definite. These authors show that this increase is very much less than the decrease in free acid and therefore cannot account for any great part of this decrease. It has been found[13] that the changes in the conductivity of the juice are practically identical with the changes in acidity and this seems to indicate that the conductivity is mainly due to the presence of free acid in the juice. The decrease in conductivity would therefore indicate that there is an actual disappearance of acid during the ripening process. The evidence in favour of the view that the process is not simply due to neutralisation of the acid by the bases present in the juice may be obtained by an examination of the relationship between ash and acid. The amount of ash may be assumed to give a very good idea of the amount of base

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present. It is found that the simple correlation coefficient between the acid and ash is -0.742. This would suggest that there is actually a direct relationship between these two factors. However, it must be remembered that the acid is negatively correlated with the sugar to which the main increase in growth may be attributed. The ash also increases in the juice during ripening and is therefore positively correlated with the sugar. When the effect due to the increasing sugar is eliminated it is found that the partial correlation between acid and ash is - 0.151. This value has no definite significance and it may be concluded that the decrease in acidity is not due simply to an increase in the basic contents of the juice together with the consequent neutralisation of free acid.

The conclusions which have so far been drawn are applicable only to the ripening period of the berry. If the conditions of growth are no longer maintained in the form, normally associated with the ripening process, a new set of factors has to be considered and the exponential law, as here derived, will no longer be applicable. Under these circumstances it would also be expected that this form of expression could not be applied to the changes during the initial growth period when the acid is increasing in amount. This stage was apparent in the 1926 results but it was only in the 1927 season that the work was commenced sufficiently early to enable any idea to be formed of the type of growth change which occurred during this initial cycle. In 1927 this stage extended over a period of about 6 - 8 weeks and sufficient data were collected. Bioletti, Cruess and Davi[(5)] find that this increase of acid is not very large but is quite definite. In one variety they found an increase of 0.67 per cent. as tartaric acid.

The data obtained in 1927 during this period are given in Table XXIII (up to the stage marked by the dotted line). When the work was commenced the berries were very small, very green and hard and, presumably, had not been formed for any length of time. They were as nearly as possible

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in the form in which they first appeared on the bunch. The total length of time from the stage at which the berries first appear until the time when the grapes begin to colour is roughly about $2\frac{1}{2}$ months and, in the present case, in accordance with this period it appears that about two weeks must have elapsed between the time of appearance of the berries and the time at which the observations were commenced. At no stage of the initial growth period was there any clear indication that the growth commenced with zero acidity. It seems unlikely that there could be such a sudden rise to over 2.0 per cent. of acid in a matter of 2 - 3 weeks. The curves do not indicate the existence of an initial rapid change of acidity.

On examining the curves the existence of a reverse curve of growth seemed evident and it became clear that the best method of expressing the changes of acidity during this period was by means of the autocatalytic equation as previously developed. Since the evidence of zero acidity was clearly lacking it would appear that this particular cycle of growth only commenced when a definite concentration of acid was already present. Under these circumstances the autocatalytic equation to be adopted must be of the form

$$\log \frac{y - c}{d - y} = K(t - t_1)$$

where "c" is the concentration of acid when the cycle of growth, represented by this equation, commences; "d" is the concentration of acid at the completion of this growth cycle, so that the total change of acid during this cycle is represented by "d - c". $K = k(d - c)$ where "k" is the velocity constant of the change "y" is the acidity at time "t" and "t_1" is the time when "y" is equal "$\frac{d + c}{2}$", i.e., "t_1" is the "half period" of this change.

The constants have been calculated from the observed data in the same way as before. The time is reckoned in days from the commencement of observation. The results are given in Table XXV

Table XXV /

TABLE XXV.

Variety.	c	d	K	t_1	k	$\frac{d - c}{K} \times 10^{-2}$
White Hanepoot.	2.50	3.55	0.0510	15.0	0.0486	20.6
Barbarossa.	2.10	3.02	0.0529	20.0	0.0576	17.4
Flaming Tokai.	2.10	3.40	0.0514	15.0	0.0395	25.3

The agreement between the observed and calculated values for the acidity is shown in Fig.9 in which the dotted portion of the curve represents the theoretical growth change prior to the beginning of observation. The point A represents the stage at which the curve of the initial growth period intersects the curve of decreasing acidity.

It is evident that during this early stage of growth there is a very great similarity in the change in acidity for all the varieties. It will be seen that the White Hanepoot variety is characterised by a higher value for both the initial and final concentration of acid for this particular cycle. The actual amount of acid produced during this cycle depends upon the variety of grape, e.g., 1.05, 0.90, 1.30 per cent. for the varieties in the order given in the table. Although the values of "K" are very similar for all the varieties it will be seen that the values of the growth velocity constant "k" vary a good deal according to the variety, a low value being associated with a high production of acid. It is clear from the comparatively high values for this constant that this cycle of growth is a relatively rapid one. The inherent differences in the characteristics of the varieties is readily brought out by a comparison of the <u>growth capacity constants</u>. This value indicates that Flaming Tokai has the greatest capacity for production of acid during this cycle. This is in accordance with the low value of "k" and the comparatively high value of "d - c" for this variety.

Prior to the onset of this growth cycle the concentration of the acid in the juice must be, at least, that given by the value of "c" in Table XXV. During the complete development of the grape, therefore, three stages must occur

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in the changes of acidity. The first stage ends with the production of "c" grams of acid per 100 c.c. of juice. The second stage consists of the increase in acidity and ends with the maximum production of "d" grams of acid. The final stage coincides with the period of ripening and ends with the minimum value of the acidity at maturity. The results, here obtained, indicate that the acidity had a value of "c" at a period of about two or three weeks prior to the commencement of observation. This period is practically coincident with the time at which the berries first begin to appear on the bunches. It can only be concluded that the actual berry is formed only when a concentration of "c" grams of acid per 100 c.c. of liquid is already present. This conclusion leads to the assumption that this must be the concentration of acid which must be present in the sap of the pedicels of the berry or in the liquid stored in the fruit-bud. When the berry is initially formed there must be a forward movement of liquid and this liquid has a concentration of "c" grams of acid. Reed[32] has pointed out that a high sap-concentration is associated with a slower growth of the shoots of fruit trees and with fruit-bud formation. The sap-concentration is higher in the apical region of the shoot than in the basal region. The assumption that the berry is initially formed by the influx of liquid is supported by the evidence afforded by the initial changes which occur in the total solids in the berry. These changes during the ripening period only commence after the proportion of total solids has reached a certain value (about 6 - 8 per cent. according to the variety). The evidence is perfectly clear that this value is attained only after an initial decrease in total solids has occurred. This can only occur on the assumption that the formation of the berry is initially dependent upon an influx of liquid and it may be concluded that this is due to a forward movement of liquid from the pedicel or from the base of the fruit-bud. The swelling and consequent formation of the berry is thus accounted for, and the required concentration of acid is produced by supposing that the acid occurs at the concentration of "c" grams per 100 c.c.

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in this liquid as it passes into the berry.

(d). TOTAL SOLIDS IN THE BERRY.

On examining the curves showing the changes in the total solids in the berry it was seen that these changes were very similar in form to those which occurred in the soluble solids. The changes in the total solids during the period of ripening did not commence from zero concentration. The simple autocatalytic equation, therefore, was modified in a manner similar to the method adopted for the soluble solids.

The change in the total solids in the berry during ripening may therefore beexpressed by means of the equation

$$\log \frac{x - c}{d - x} = K(t - t_1)$$

and the rate of growth by

$$\frac{dx}{dt} = k(x - c)(d - x)$$

where $K = k(d - c)$ and "t_1" is the "half period" when $x = \frac{d + c}{2}$.

The constants in these expressions have the same general significance as in the case of the soluble solids in the juice. "d" represents the final yield of dry matter in the berry and is the resultant of two growth cycles. The first growth cycle is completed by the production of "c" grams of dry material per 100 grams of berry and the second growth cycle, as represented by the above equation, is characterised by the further formation of "d - c" grams of dry matter.

The data for the total solids for the seasons 1925, 1926 and 1927 are given in Tables XXVI - XXVIII. The data for 1923 have been excluded since facilities were not available for an accurate determination of this quantity. The total solids have been expressed in terms of dry weight per 100 grams of berry.

Table XXVI /

TABLE XXVI.

Grapes from Constantia during 1925 Season.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28. 1.25	13.65	12.57	10.81	10.60	11.57	12.47
4. 2.25	14.84	13.46	10.64	11.71	13.45	13.61
11. 2.25	16.31	16.25	12.99	12.79	15.48	15.68
18. 2.25	17.35	19.27	14.82	14.30	17.44	18.84
25. 2.25	19.70	18.75	16.45	17.38	20.62	17.08
4. 3.25	21.12	21.13	18.78	18.62	18.25	19.52
11. 3.25	21.52	20.93	19.28	18.79	19.43	21.47

TABLE XXVII.

Grapes from Constantia during 1926 Season.

Date.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
13. 1.26	7.88	8.00	8.46	8.98	9.97	8.91
20. 1.26	8.72	9.58	7.91	9.27	10.46	9.27
27. 1.26	10.86	10.79	8.89	9.13	12.55	10.48
3. 2.26	12.84	13.35	10.04	11.22	13.04	10.67
10. 2.26	13.73	16.02	13.38	12.20	15.66	11.79
17. 2.26	16.81	16.90	15.99	14.53	15.50	14.76
24. 2.26	18.30	18.95	17.39	18.04	16.86	17.69
3. 3.26	20.53	21.16	17.90	19.03	20.43	18.27
10. 3.26	24.04	22.06	19.32	20.16	-	21.07
17. 3.26	23.36	21.94	18.86	22.13	-	19.69
24. 3.26	23.28	23.54	19.68	-	-	21.05

Table XXVIII /

TABLE XXVIII.

Grapes from Paarl during the 1927 Season.

Date.	White Hanepoot.	Barbarossa.	Flaming Tokai.
30.11.26	9.54	8.71	11.54
7.12.26	6.88	8.18	7.28
14.12.26	7.25	6.99	7.11
21.12.26	7.73	7.39	7.34
28.12.26	8.07	7.93	7.64
4. 1.27	9.43	8.46	8.26
11. 1.27	10.19	8.58	9.09
18. 1.27	12.32	9.64	11.94
25. 1.27	13.63	10.75	12.25
1. 2.27	15.31	12.30	14.33
8. 2.27	15.21	13.65	14.49
15. 2.27	18.88	17.47	16.51
22. 2.27	19.77	17.48	17.38
1. 3.27	21.64	19.91	19.94
8. 3.27	21.81	18.65	20.02
15. 3.27	22.89	19.56	19.95
22. 3.27	24.83	20.53	20.93
29. 3.27	24.10	20.05	21.86

The general course of the changes in the total solids in the berry is very similar to the course of the changes in the soluble solids in the juice. The constants for the equation have been calculated from the observed data and are given in Table XXIX. The time is reckoned in days from the commencement of the investigation in each season and logarithms to the base 10 were used.

Table XXIX /

TABLE XXIX.

Total Solids in the Berry_ $\log \frac{x - c}{d - x} = K(t - t_1)$.

Locality.	Variety.	Year.	c	d	K	t_1
Constantia.	White Hanepoot.	1925	5.70	22.70	0.0326	6.5
		1926	6.05	24.80	0.0325	32.0
	Red Hanepoot.	1925	6.30	22.35	0.0318	7.0
		1926	6.25	24.05	0.0322	28.0
	Gros Maroc.	1925	6.90	21.20	0.0330	16.5
		1926	6.72	20.43	0.0365	30.0
	Barbarossa.	1925	5.85	20.35	0.0321	12.0
		1926	6.43	22.55	0.0345	33.0
	Waltham Cross.	1925	7.00	22.40	0.0303	12.0
		1926	6.85	21.60	0.0301	22.0
	Flaming Tokai.	1925	7.88	22.82	0.0342	13.5
		1926	7.92	22.10	0.0353	35.0
Paarl.	White Hanepoot.	1927	6.12	25.62	0.0231	66.5
	Barbarossa.	1927	6.45	21.50	0.0259	70.5
	Flaming Tokai.	1927	6.75	22.55	0.0261	68.5

When these expressions are plotted the close agreement between the observed and calculated values can be seen. In Fig.10 the curves for the results obtained for Paarl grapes are given. The close resemblance to the curves for the soluble solids can be seen. From Table XXIX it will be seen that the first growth cycle ends with the formation of about 6 - 8 per cent. of dry matter before the second cycle commences. The value of this quantity varies slightly according to the variety of grape, being highest in the case of Flaming Tokai, but there does not seem to be any great difference between the corresponding varieties grown at Paarl and Constantia.

On examination of Table XXVIII and by reference to Fig.10 it can be clearly seen that during the first growth cycle the total solids decrease to a minimum value before the increase, corresponding to the second growth cycle as here given,

becomes /

becomes evident. This initial decrease is not evident in the work of previous seasons owing to the relatively later stage at which the observations were commenced. The results have, however, been calculated on the assumption that such a change must have occurred. This minimum value is represented by "c" grams of dry matter per 100 grams of berry and it would therefore seem that, in the initial stages of formation of the berry, the main process must be an absorption of liquid. The concentration of solids in this liquid cannot be sufficiently great to cause a concomitant increase in the total solids in the berry. This process is initially very rapid and any possible production of solid matter is completely masked by the process of dilution which is taking place. The existence of a similar effect is evident to a slight extent in the case of the soluble solids but it is not clearly defined. The process of dilution in this case is apparently balanced by the concurrent accretion of soluble material. In neither case, however, is it possible from the data to define the exact course of the change.

It will be seen from Table XXIX that, on comparing the values of "t_1", for the different seasons for each variety, the same division into early and late ripening varieties is again possible. On comparing the value of "t_1" with the corresponding value for the soluble solids it will be seen that the "half period" for the total solid transformation is practically coincident with that for the soluble solids. This indicates that the maximum growth rate occurs at practically the same time for both factors and that the "grand period of growth" for the second cycle in the total solids is practically the same as that for the second cycle of the soluble solids. This similarity in the times during which these two factors change indicates an underlying similarity in the causes which bring about the changes in these factors. The changes in both cases are probably due to the changes which occur in the sugar and acid content of the juice of the berry.

In the case of the values for the final crop yield and for "K" the same remarks are applicable as in the case of the corresponding quantities for the soluble solids. The effect of seasonal conditions upon the value of "K" is small while the effect of changes in environment is again noticeable. The value of "K" at Paarl is relatively smaller than the corresponding value for Constantia. As an index for comparison, the values of "k," the growth velocity constant, and of "$\frac{d - c}{K}$", the growth capacity constant, for the second cycle, may be taken. The values obtained from the experimental data are given inTable XXX.

TABLE XXX.

Locality.	Variety.	Year.	k	$\frac{d - c}{K} \times 10^{-2}$
Constantia.	White Hanepoot.	1925	0.00192	5.21
		1926	0.00178	5.62
	Red Hanepoot.	1925	0.00190	5.26
		1926	0.00181	5.53
	Gros Maroc.	1925	0.00231	4.33
		1926	0.00266	3.76
	Barbarossa.	1925	0.00222	4.51
		1926	0.00214	4.67
	Waltham Cross.	1925	0.00197	5.08
		1926	0.00204	4.90
	Flaming Tokai.	1925	0.00230	4.35
		1926	0.00248	4.03
Paarl.	White Hanepoot.	1927	0.00118	8.44
	Barbarossa.	1927	0.00172	5.81
	Flaming Tokai.	1927	0.00166	6.02

From this table it will be ssen that a high growth capacity is associated with a low value of "k", or that a high crop yield is associated with a long growing period. There are slight variations in "k" according to seasonal conditions but these are insignificant when compared with the effect due to changes in locality. The latter have a much greater effect upon the "internal" factors governing the growth of the plant.

On comparing the values of "k" for the total

solids /

solids with the corresponding values for the soluble solids, it will be seen that the two values are practically the same. Therefore it would seem that the changes which occur in the total solids are mainly due to the changes which occur in the soluble solids. These latter in turn are mainly due to the changes which occur in the sugar and acid content of the juice. It has been shown that the changes in acidity are relatively small in comparison with the changes in the sugar content of the juice. During the ripening period, therefore, the changes in the sugar content of the juice are relatively of such magnitude that they are practically the cause of the whole of the second cycle of growth in the berry. It has already been shown that the relationship between the soluble solids and sugar in the juice is so close that it may be expressed by a simple linear function. However, on account of the difficulty of determining the exact amount of juice in the berry, it is not possible to work out an expression for the relationship between the total solids and the soluble solids or sugar in the same way as for these two latter factors. At the same time it must be remembered that changes also take place in the seeds and skins of the berry during ripening. However, the magnitude of the constants indicate that probably a linear relationship also exists between the total solids of the berry and the sugar content of the juice. As evidence of this, the correlation coefficient between these two factors for the total number of determinations for all the seasons has been found to be + 0.976. This is extremely high and is clear proof of the dependence of the total solids upon the sugar content of the juice. That the relationship is practically linear is shown in Fig.11 where the mean values of the sugar content have been plotted for every unit difference in the total solids. The importance of the changes in sugar content of the berry during ripening is therefore clear.

All the facts so far elucidated show that the growth constants for the various factors possess equal significance, and that they are all influenced in the same way so that effects due to external conditions are not limited to a single factor /

factor. The growth constants are all more significantly affected by changes in locality than by changes in climatic conditions. When the values of the constants for any given locality are considered it will be seen that they are genetically significant for the different varieties and therefore they afford, under comparable conditions of growth, a specific means of comparison between different varieties. When the values for a given variety are considered it is clear that they are directly affected by changes in environment and therefore the changes in the values of the constants should be a measure of the variation in external conditions. It is clear that Robertson's idea that "k" is an inherent specific constant, independent of environmental conditions, cannot be upheld in the case of plants. It can only be concluded that, in the case of animals, some mechanism must exist which counteracts the effects due to changes in environment. Such mechanism must be absent in plants.

(e). RELATIONSHIP BETWEEN SUGAR AND ACID IN THE JUICE.

In all the work carried out on the changes occurring during the ripening of grapes, it has been shown that the most important changes are those which take place in the sugar and acid content of the juice. The remaining changes are subordinated by those which occur in these two factors. At the same time it can be clearly seen that a close relationship must exist between these two factors, such that a high content of sugar is associated with a low content of acid and vice versa. It would appear that those conditions which favour the formation of sugar simultaneously favour a reduction in the acid content of the juice. These facts have been emphasized by other workers. Caldwell(9), for example, in his paper states that "there is a consistent and fairly high degree of correlation between sugar, acid and total astringent content of the juice". Bioletti, Cruess and Davi(5) also draw attention to this fact and attempt to express the relationship by stating that "during <u>ripening</u> the sugar curve ...... is more or less the mirror image of the total acid curve multiplied by five, i.e., increases

as /

as the acid decreases." It is therefore clear that the relationship between the sugar and acid content of the juice must be an inverse one. The relationship, however, does not appear to be a direct inverse ratio.

As evidence of the close relationship between the acidity and sugar, the coefficient of correlation has been calculated for each variety. In every case this value was obtained by combining the experimental data obtained for each variety grown at Constantia for each of the seasons. In addition, the data for both White and Red Hanepoots have been combined. The reasons for this step have already been given. The following coefficients were obtained :-

Hanepoot	-0.914 ± .025
Gros Maroc..	-0.992 ± .005
Barbarossa..	-0.914 ± .038
Waltham Cross	-0.940 ± .030
Flaming Tokai	-0.939 ± .026

These values were calculated from the data obtained during the ripening period, i.e., while the acid was decreasing. They indicate an extremely high degree of negative correlation and their magnitude is the same for all varieties. The regression lines are not, however, linear as can be readily seen by plotting the acid against the sugar. It can also be proved that the deviations from the line representing the direct inverse ratio are significant.

The type of curve showing the change of acid with sugar is shown in Fig.12 where the values for the Hanepoot grapes from Constantia are employed as embodying the most complete set of data. The curve decreases as the sugar increases and is convex towards the sugar-axis. The curves are only applicable over the range of the ripening period, i.e, while the acid is decreasing. The values of the sugar content at the stage of initial decrease of acid are very similar for all the varieties of grapes, but the limit of maximum sugar content varies slightly according to the variety of grape.

During /

During the period of decrease of acidity the change in the acid content of the juice is given by

$$\log \frac{a}{y - a} = k_1(t - t_1) \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

while the change in the sugar content of the juice is given by

$$\log \frac{x}{b - x} = K_2(t - t_2) \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where the constants have the significance already given to them.

By eliminating t from these two expressions the following relationship is obtained

$$\log \frac{\alpha a}{y - a} = \frac{k_1}{K_2} \log \frac{\beta x}{b - x} \quad \ldots\ldots\ldots\ldots \quad (3)$$

where $\log \alpha = k_1 t_1$ and $\log \beta = K_2 t_2$

On simplification equation (3) becomes

$$(y - a)^n = A_1 \left(\frac{b - x}{x}\right)$$

or $(y - a)^n = \frac{A}{x} - B$ where $n = \frac{K_2}{k_1}$

This gives an expression indicating the relationship between the sugar and acid in the juice. In practice, it has been found that the value of "n" is slightly less than the theoretical value given above. In this particular case, the period of change is limited to <u>the period of decreasing acid</u> so that under these conditions the total change in the sugar content will be "b - s" where "s" is the sugar content at the stage when the acid commences to decrease. On account of this limitation n will tend to be slightly smaller than the value given by "$\frac{K_2}{k_1}$" or "$\frac{k_2 b}{k_1}$", being more nearly equal to $\frac{k_2(b - s)}{k_1}$.

The values of the constant "n" may be solved graphically by using the expression in the form

$$n \log (y - a) = c - \log x + \log (b - x)$$

and A and B may then be corrected by the method of least squares. The results obtained in this way are given in Table XXXI.

Table XXXI /

TABLE XXXI.

Locality.	Variety.	a	n	A	B	Limits of Sugar.
Constantia.	Hanepoot.	0.35	1.30	29.22	1.27	6 - 22 %
	Gros Maroc.	0.55	1.45	33.76	1.65	5 - 20 %
	Barbarossa.	0.40	1.20	26.00	1.32	6 - 19 %
	Waltham Cross.	0.50	1.23	18.28	0.87	5 - 20 %
	Flaming Tokai.	0.45	1.20	29.47	1.38	6 - 19 %
Paarl.	White Hanepoot.	0.40	0.90	17.80	0.77	6 - 24 %
	Barbarossa.	0.40	1.40	15.00	0.89	4 - 19 %
	Flaming Tokai	0.36	1.20	17.20	1.05	4 - 18 %

If the calculated and observed data were plotted in the form of a curve, it would be seen that the agreement between the results was extremely good. Since, in the case of grapes grown at Constantia, the results are calculated on the basis of the whole data for three seasons it is clear that, under constant cultural conditions in one locality, the variations for any particular variety must be within comparatively narrow limits. It may be concluded that the sugar and acid in the juice do not fluctuate entirely independently of each other. Under such conditions it would seem that the factors which determine the chemical character of the crop are those which influence the photosynthetic activity of the plant. Any condition which favours the production of sugar brings about at the same time a decrease in the acidity, the magnitude of which is related to the amount of sugar which is produced. These conclusions are in agreement with those drawn by Caldwell[9] in his paper.

Under the same cultural conditions in the same locality it has been shown that the values of "K" and "k" vary within comparatively narrow limits so that the value of "n" is practically constant. Seasonal conditions do not produce large variations in the growth constants and equable climatic conditions must tend towards the production of a uniform crop.

In /

In these circumstances it should be possible to predict with some degree of certainty the chemical character of the crop. It has already been pointed out that Gregory[20] has found in the case of barley that net assimilation and leaf-growth rate are positively and negatively correlated respectively with total radiation so that a mechanism is provided for maintaining the yield of the plant within fairly narrow limits in spite of climatic variation. When the effects due to changes in locality are studied it will be at once seen by reference to Table XXXI that the constants for the Paarl grapes differ from those for the same varieties at Constantia. This is in accordance with the fact that the constants "K" and "k" are directly affected by changes in locality. In this connection the remarks of Caldwell[9] are significant. This worker states that fluctuations in the composition of a given variety in the same locality year after year, even with wide differences in seasonal conditions, are very much narrower than in the same variety grown over a wide area under a diversity of soil and cultural conditions.

In practice, the application of the equation in the form given above is attended with a good deal of difficulty owing to the presence of the exponent "n". On this account it was deemed advisable to simplify the formula somewhat, even at the expense of losing the advantage which may be obtained by being able to attach a definite and special significance to the constants involved. The equation, as given, indicates the existence of an inverse relationship and may be expanded in the form

$$y = a + \frac{b}{x} + \frac{c}{x^2}$$

(neglecting higher powers of $\frac{1}{x}$)

In this form the inverse relationship is still clear and it is now possible to determine the acidity more readily from a knowledge of the sugar content of the juice. It has already been shown that the sugar may be easily estimated from the Balling degrees of the juice. In this way a knowledge

of /

of both the sugar and acid content of the juice becomes available from the simple Balling reading.

In practice, it has been found that the equation takes the form

$$y = \frac{b}{x} - \frac{c}{x^2} - a$$

The values of the constants for the different varieties, calculated from the experimental data, are given in Table XXXII. It must be remembered that this equation is only applicable over the same period as the one previously given, i.e., during the period of decreasing acid.

TABLE XXXII.

Locality.	Variety.	a	b	c.
Constantia.	Hanepoot.	0.760	29.45	24.93
	Gros Maroc.	1.010	38.65	84.10
	Barbarossa.	1.296	37.56	80.77
	Waltham Cross.	0.491	22.62	27.65
	Flaming Tokai.	1.104	35.88	59.18
Paarl.	White Hanepoot.	0.496	20.65	8.41
	Barbarossa.	0.600	20.00	32.38
	Flaming Tokai.	0.490	15.26	1.75

The lower limit of sugar is the same as given in Table XXXI since the equation only applies to the period of decreasing acid. The agreement between the observed and calculated values is shown in Fig.12 in the case of the Hanepoot varieties from Constantia. It will be seen that those varieties which are characterised at maturity by a high sugar content and a low acidity have comparatively low values for the constants. On comparison of the constants for Paarl and Constantia grapes the influence of environment can be readily seen to have a direct influence upon the growth of the berry. The values of the constants are all numerically greater for the Constantia grapes. This result might be expected from the fact that the acidity tends to be lower and the sugar

content /

content higher at Paarl than at Constantia.

In connection with the relationship between the acid and sugar content of fruit juices, the ratio of the acid and sugar content is a factor which has been used by a large number of workers in the study of an enormous variety of fruits. This ratio has generally been regarded as of great importance in evaluating the quality of a fruit. In the case of grapes, as the fruit ripens, the sugar increases and the acid decreases, so that the value of the ratio - acid : sugar - decreases. Finally, at maturity, a balance is reached and each variety, at maturity, is characterised by a given value for this ratio.

In the present instance the value of this ratio for the different varieties of grapes may be determined at any stage of the ripening process by means of the above equation. If "x" and "y" be the sugar and acid content of the juice the ratio will be $r = \frac{y}{x}$

Therefore $rx = \frac{b}{x} - \frac{c}{x^2} - a$

In this form the ratio is expressed in terms of the sugar and this is the most convenient method. It is therefore possible, from a knowledge of the sugar content, to determine either the ratio or the acidity of the juice. This information can therefore be readily obtained from a determination of the Balling degrees of the juice, from which, it has been shown, it is possible to estimate the sugar content of the juice.

The agreement between the observed and calculated values of the ratio is shown in Fig.13 for Hanepoot grapes from Constantia, the constants used being those given in Table XXXII. In practice, of course, each variety at maturity is characterised by a different value for this ratio and this value will be correlated with the characteristic flavour of the fruit. Those varieties with a mild sweet flavour will have a high sugar content and a low acidity and will consequently be associated with a low value for the

ratio /

ratio. In this way the different varieties may be grouped according to the magnitude of this ratio and it may be concluded that values with a fairly constant ratio at maturity are most to be desired. At the same time it must be borne in mind that grapes in which the acid content of the juice is too low will have a mild but somewhat insipid taste. When the various varieties are fully ripe the values of the ratio may be taken as 0.020, 0.050, 0.025, 0.028 and 0.030 for the varieties in the order given in Table XXXII. Tietz[35] in a paper on "An Important Characteristic of Cape Wines" has reported as the <u>lowest</u> ratio for Hanepoot grapes a value of 0.030. This is a somewhat higher figure than the value obtained during the present work for the same variety. Caldwell[9] has pointed out that the average value of this ratio in the case of Concord grapes is 0.067 and since this is the most generally available grape for the manufacture of commercial grape juice he concludes that this acid : sugar ratio represents that condition of a grape which most people find agreeable. Assuming that a similar state exists in the case of grapes grown in South Africa it is found that, for the varieties here investigated, the grape juices will have this ratio when the sugar content is approximately as follows :- 15.6, 16.0, 14.2, 14.4, 15.2 per cent. for the order given in Table XXXII. The corresponding Balling degrees of the juice at 20°C. will be :- 17.0, 17.2, 15.8, 15.9 and 16.5° for the varieties in the same order. These results agree closely with figures which have been independently arrived at and have been reported in another paper[13]. It would appear that in the case of export grapes the setting of a standard by reference to the Balling reading of the juice would be quite practicable. In such a case the limits would be 16 - 17° for the juice according to the variety. So far as the practical determination of this quantity is concerned, the precautions that must be taken have already been emphasized. At the same time it will readily be seen that, in the case of the sugar content and acidity of the juice, the changes which occur during the ripening of the grape may be easily followed by means of the simple reading of the

Balling /

Balling degrees of the juice. The sugar and acid can then be estimated by the methods which have been outlined.

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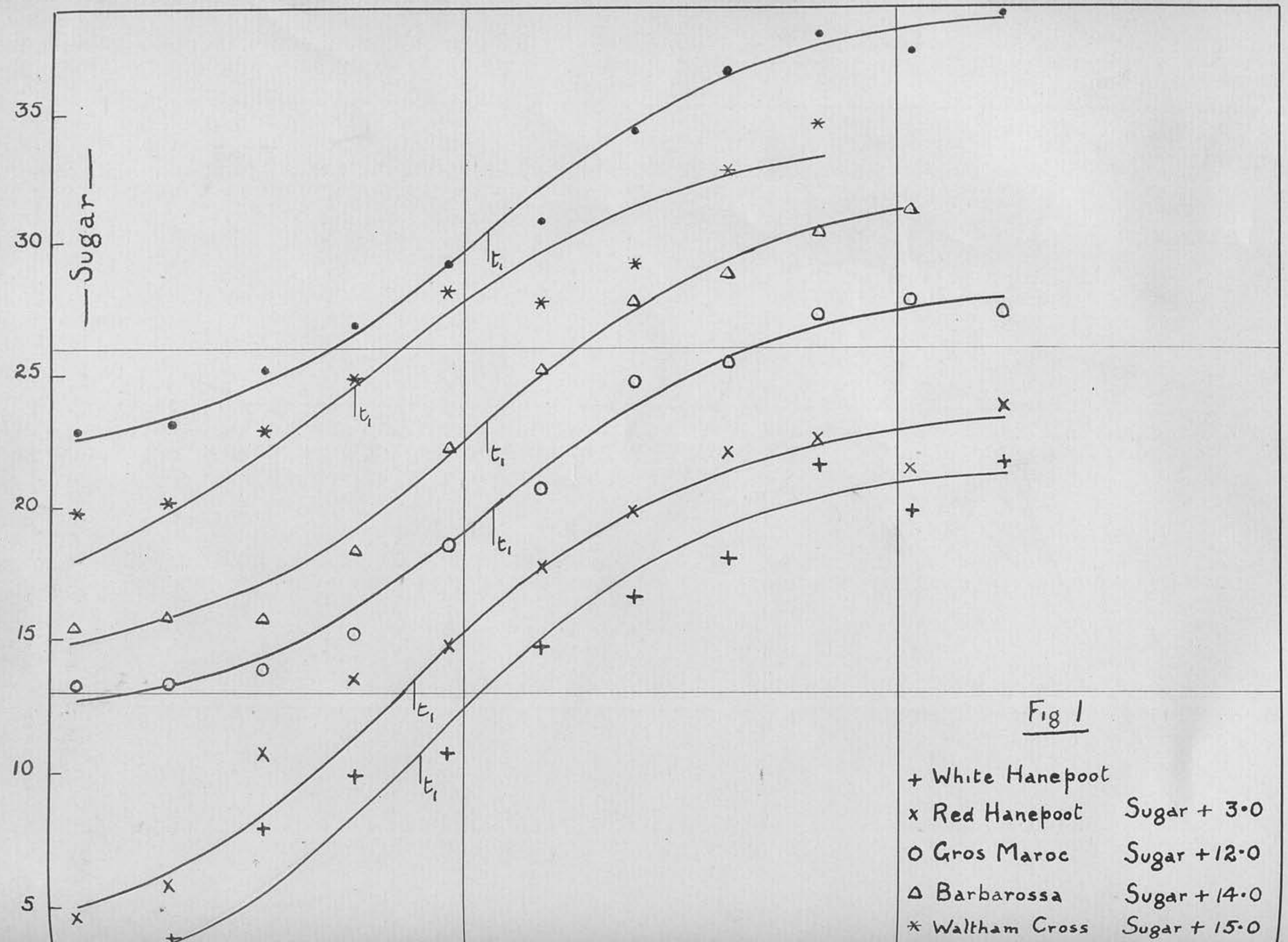


—Sugar—
35
30
25
20
15
10
5
t_1
+ White Hanepoot
x Red Hanepoot Sugar + 3·0
O Gros Maroc Sugar + 12·0
Δ Barbarossa Sugar + 14·0
* Waltham Cross Sugar + 15·0

Fig 1

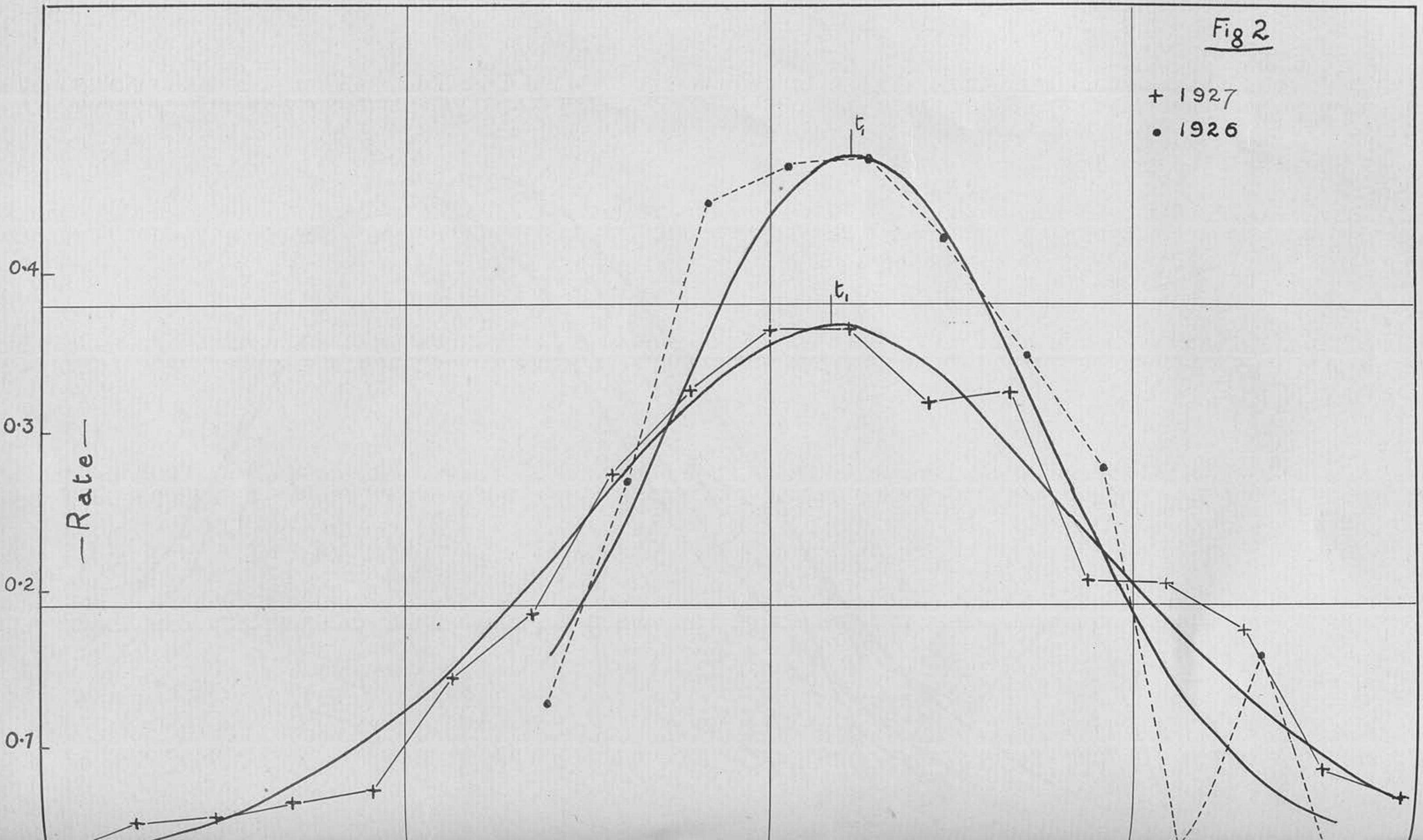


Fig 2

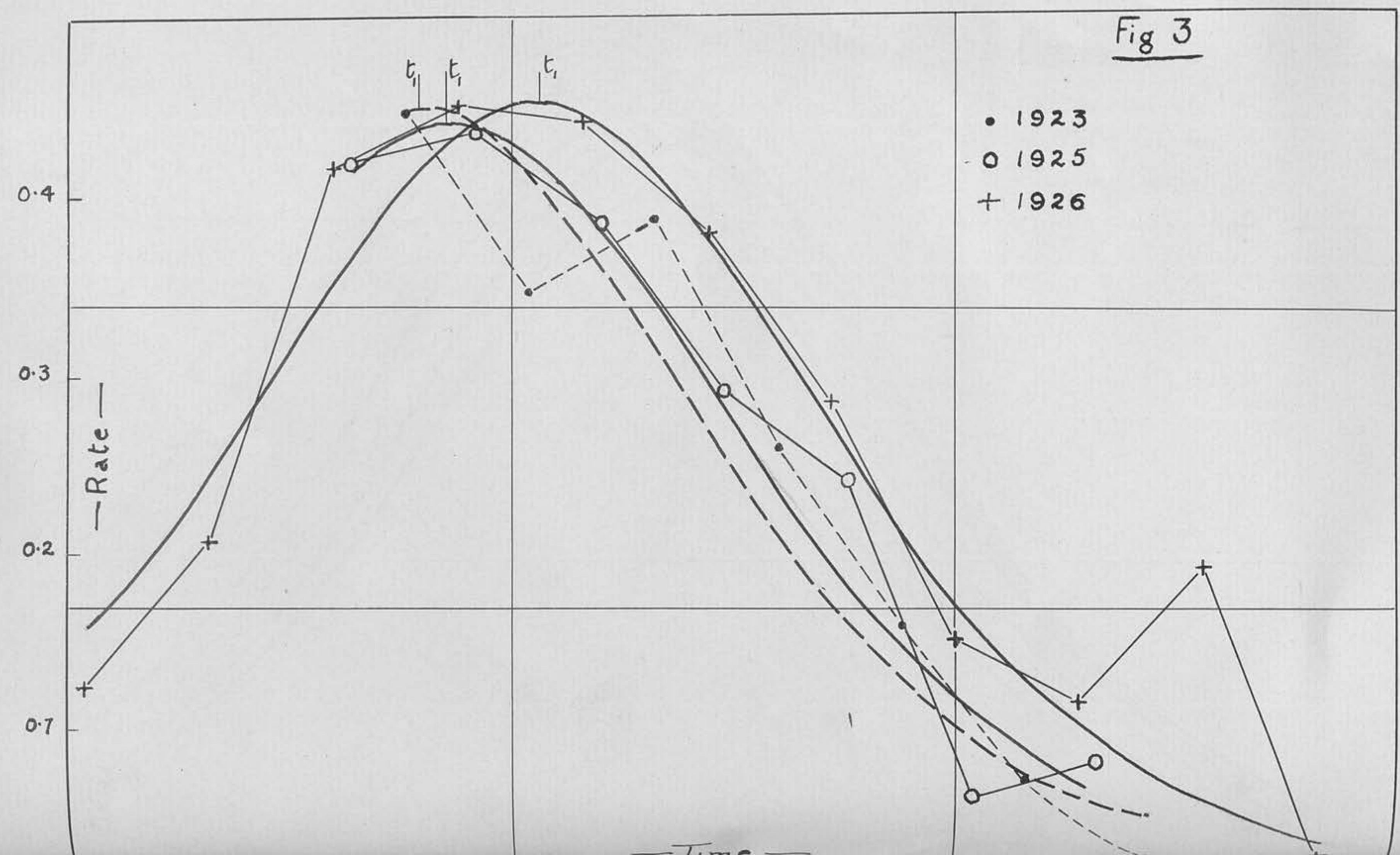


Fig 3

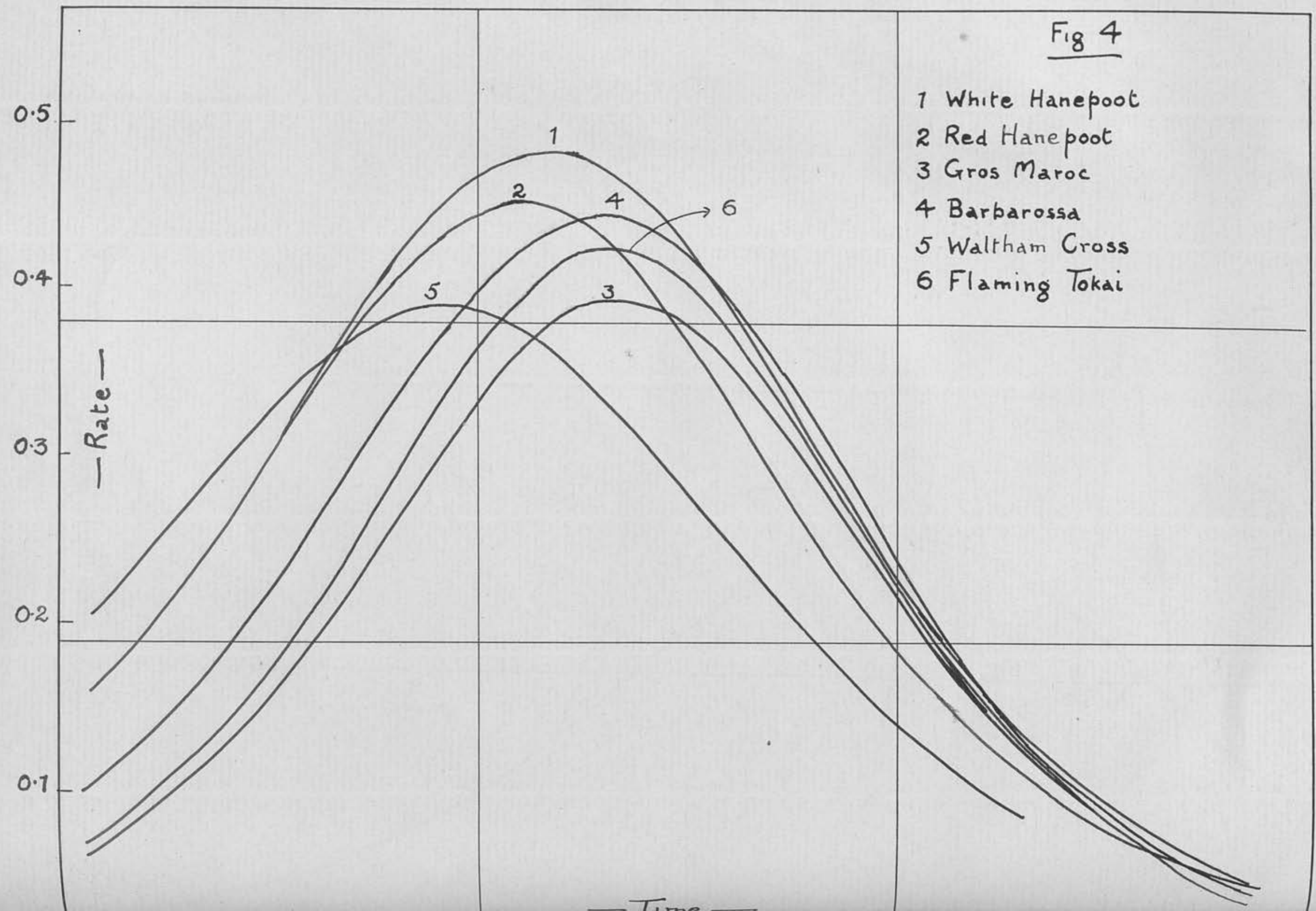
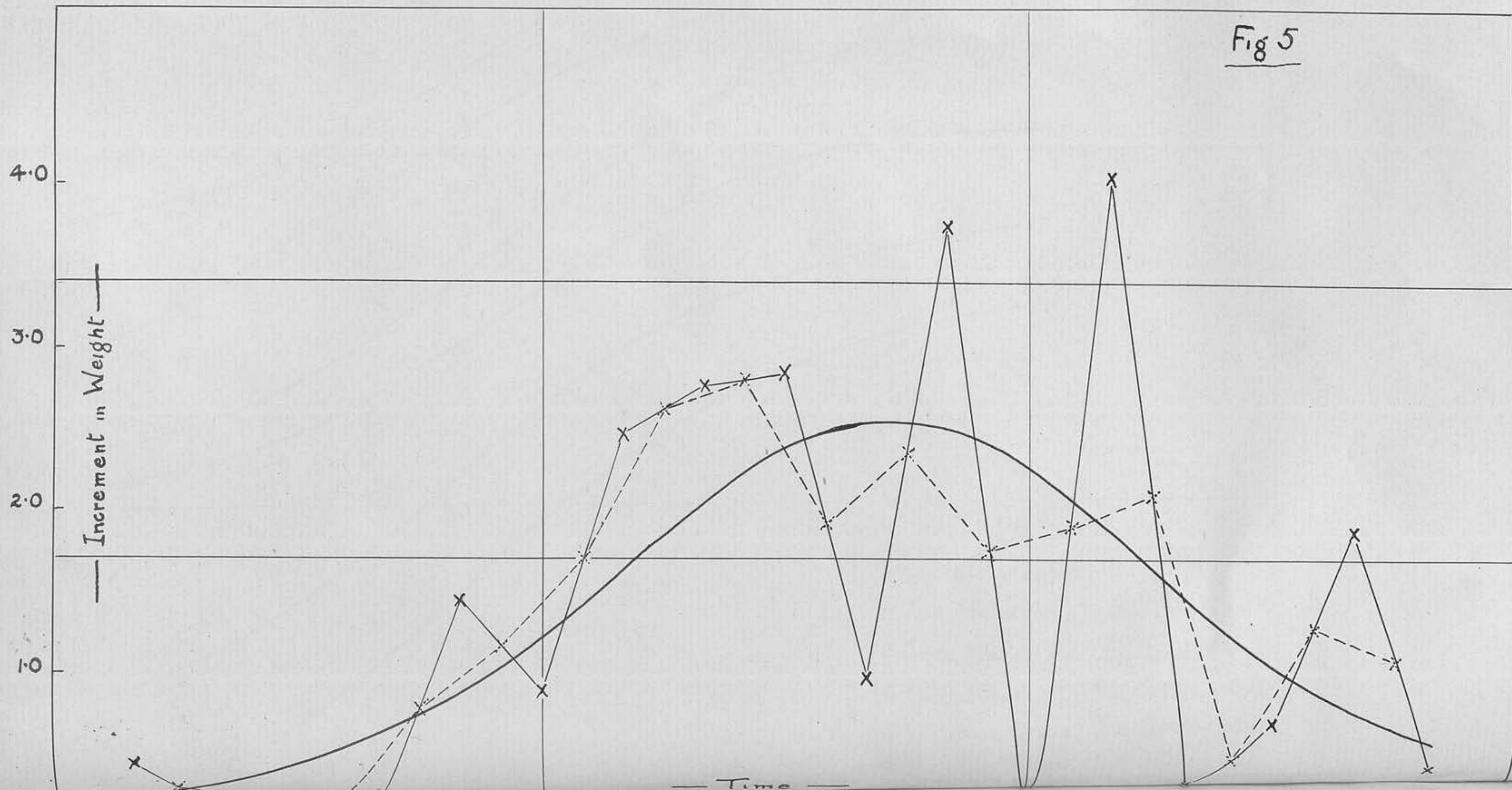
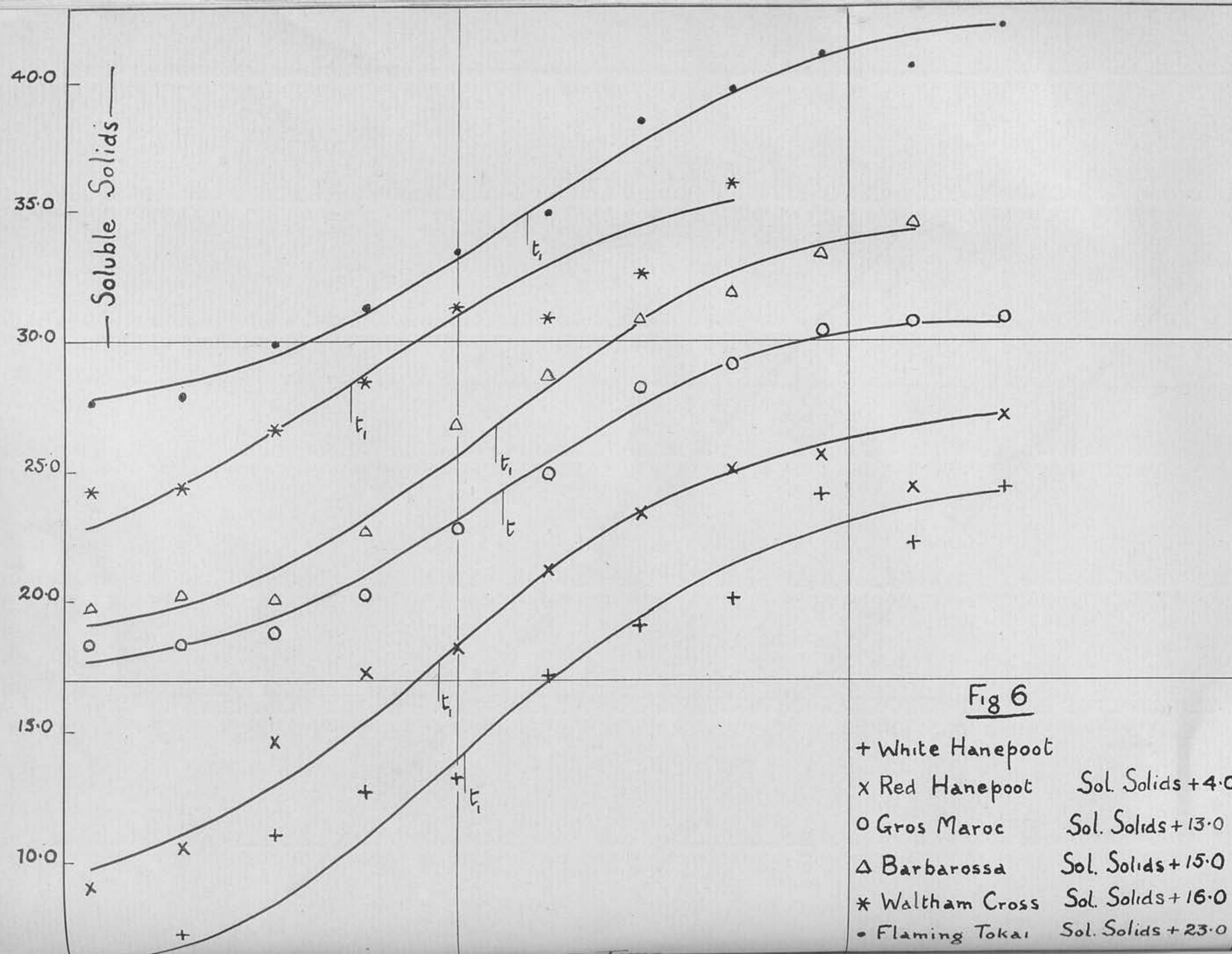


Fig 4
1 White Hanepoot
2 Red Hanepoot
3 Gros Maroc
4 Barbarossa
5 Waltham Cross
6 Flaming Tokai
0·5
0·4
0·3
0·2
0·1
— Rate —
1
2
3
4
5
6

Fig 5





Soluble Solids
40·0
35·0
30·0
25·0
20·0
15·0
10·0
t₁
t
+ White Hanepoot
x Red Hanepoot Sol. Solids + 4·0
o Gros Maroc Sol. Solids + 13·0
Δ Barbarossa Sol. Solids + 15·0
* Waltham Cross Sol. Solids + 16·0
• Flaming Tokai Sol. Solids + 23·0

Fig 6

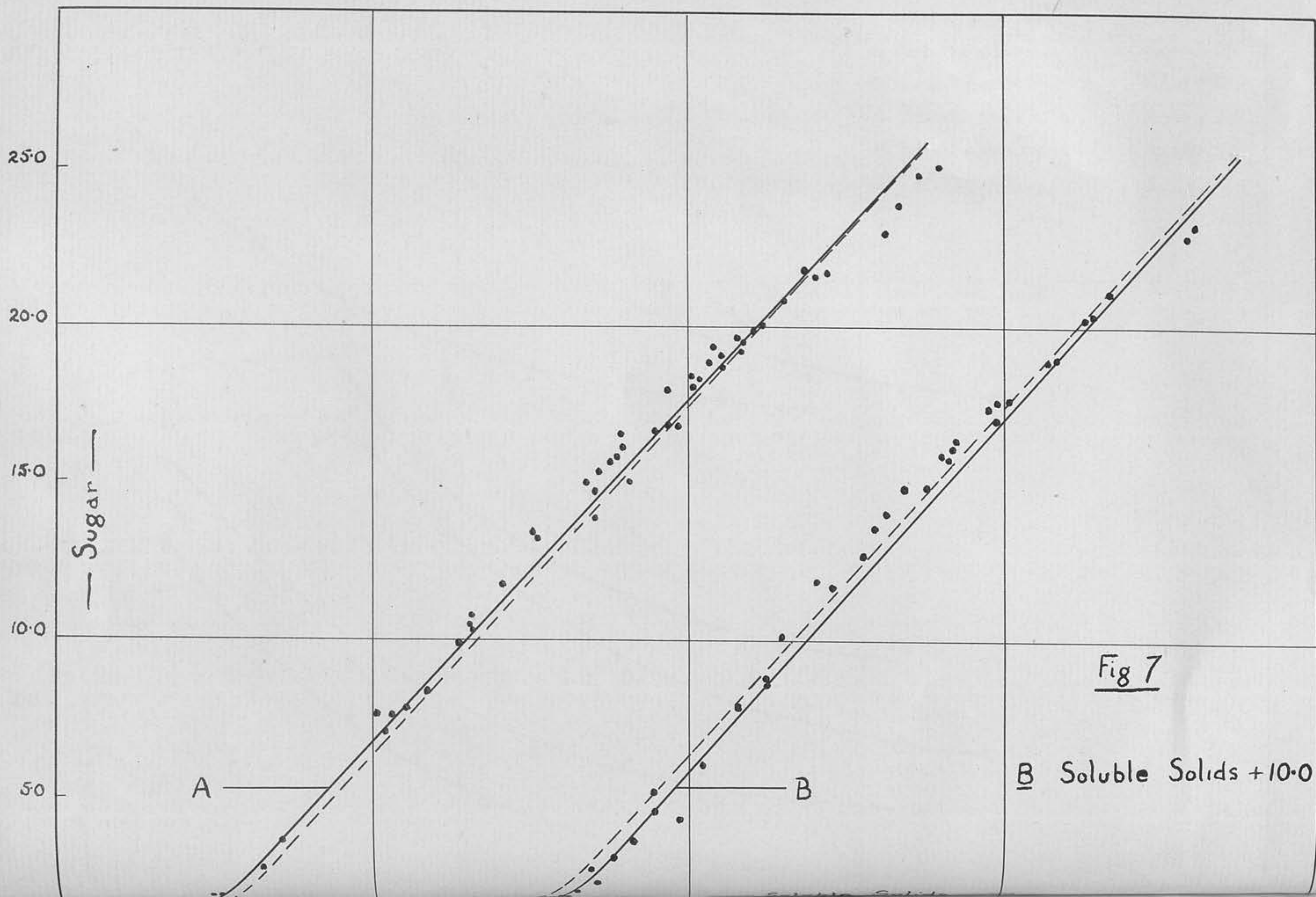


Fig 7

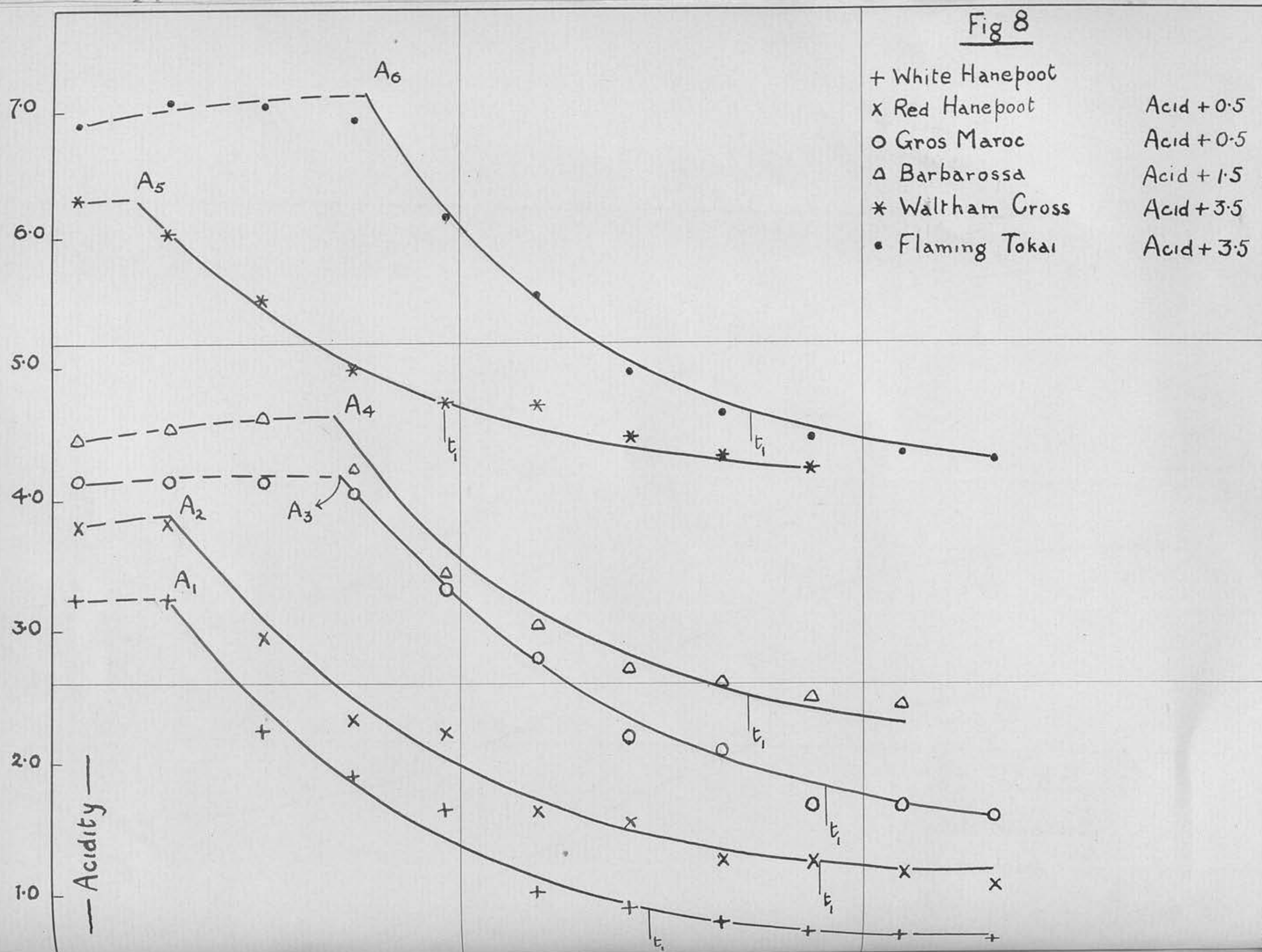
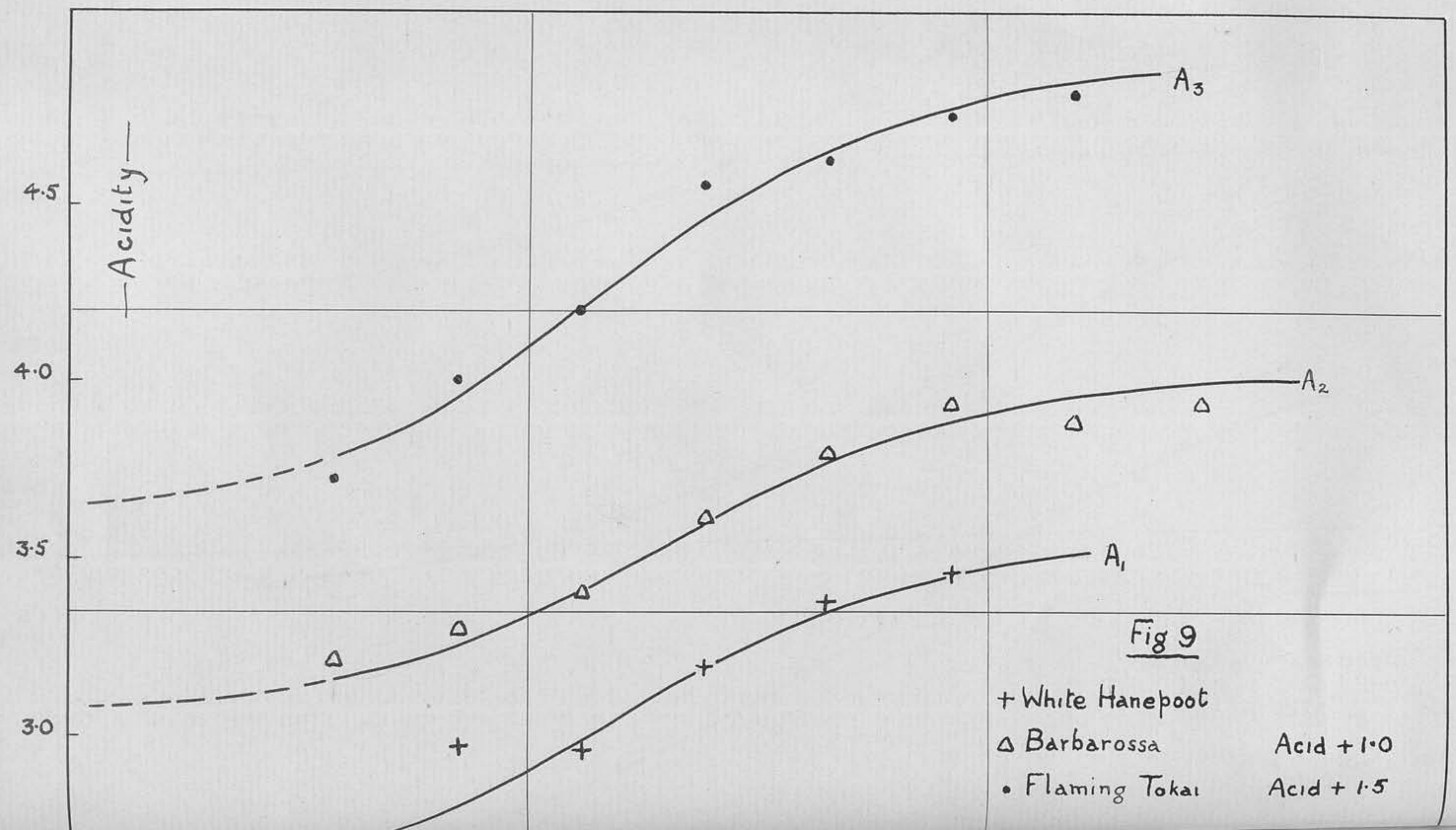


Fig 8
+ White Hanepoot
x Red Hanepoot Acid + 0·5
o Gros Maroc Acid + 0·5
Δ Barbarossa Acid + 1·5
* Waltham Cross Acid + 3·5
• Flaming Tokai Acid + 3·5
7·0
6·0
5·0
4·0
3·0
2·0
1·0
— Acidity —
A1
A2
A3
A4
A5
A6
t1



4.5
4.0
3.5
3.0
—Acidity—
A_3
A_2
A_1
+ White Hanepoot
Δ Barbarossa Acid + 1·0
• Flaming Tokai Acid + 1·5

Fig 9

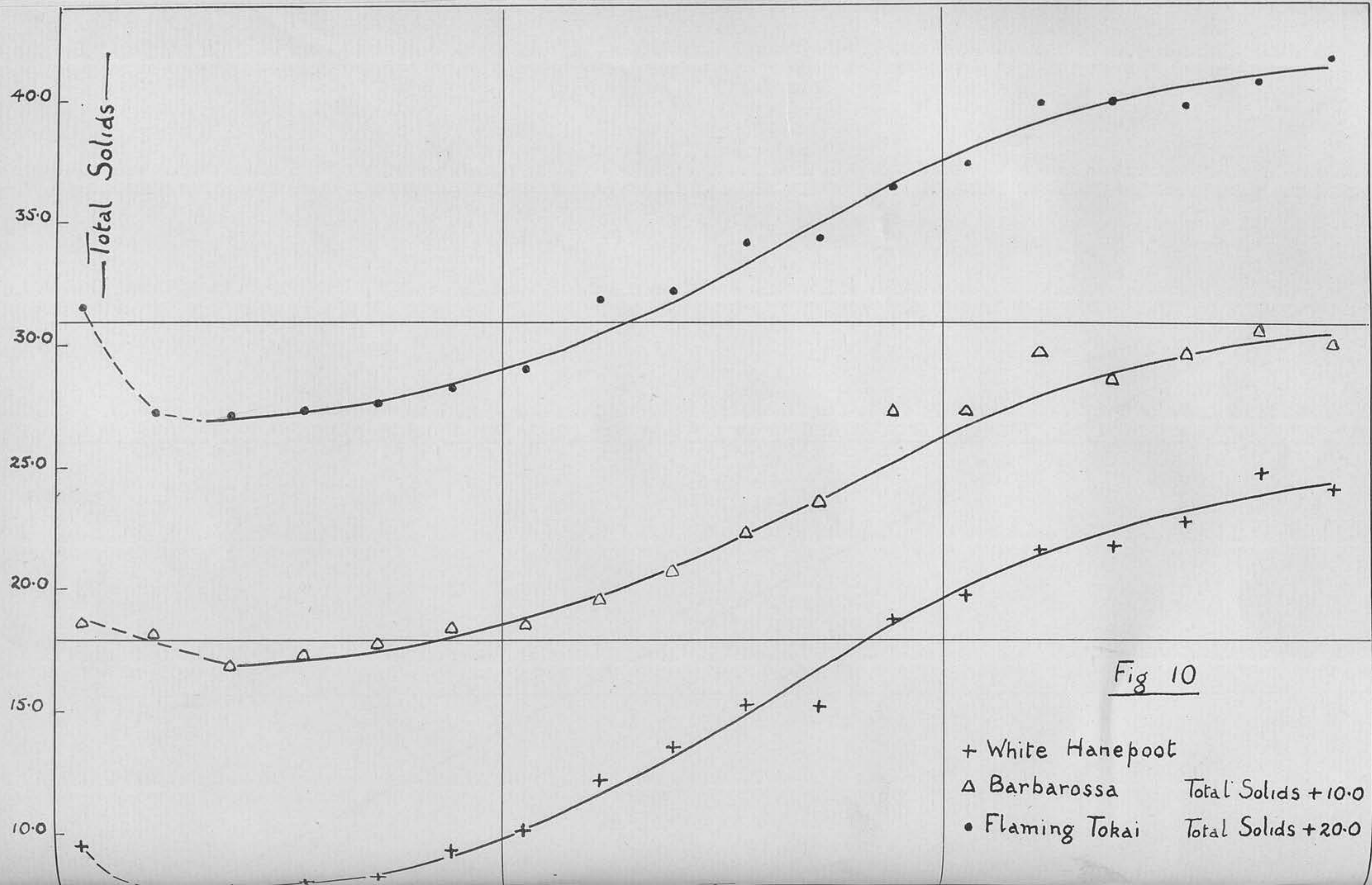

Total Solids
40·0
35·0
30·0
25·0
20·0
15·0
10·0
+ White Hanepoot
Δ Barbarossa Total Solids + 10·0
• Flaming Tokai Total Solids + 20·0

Fig 10

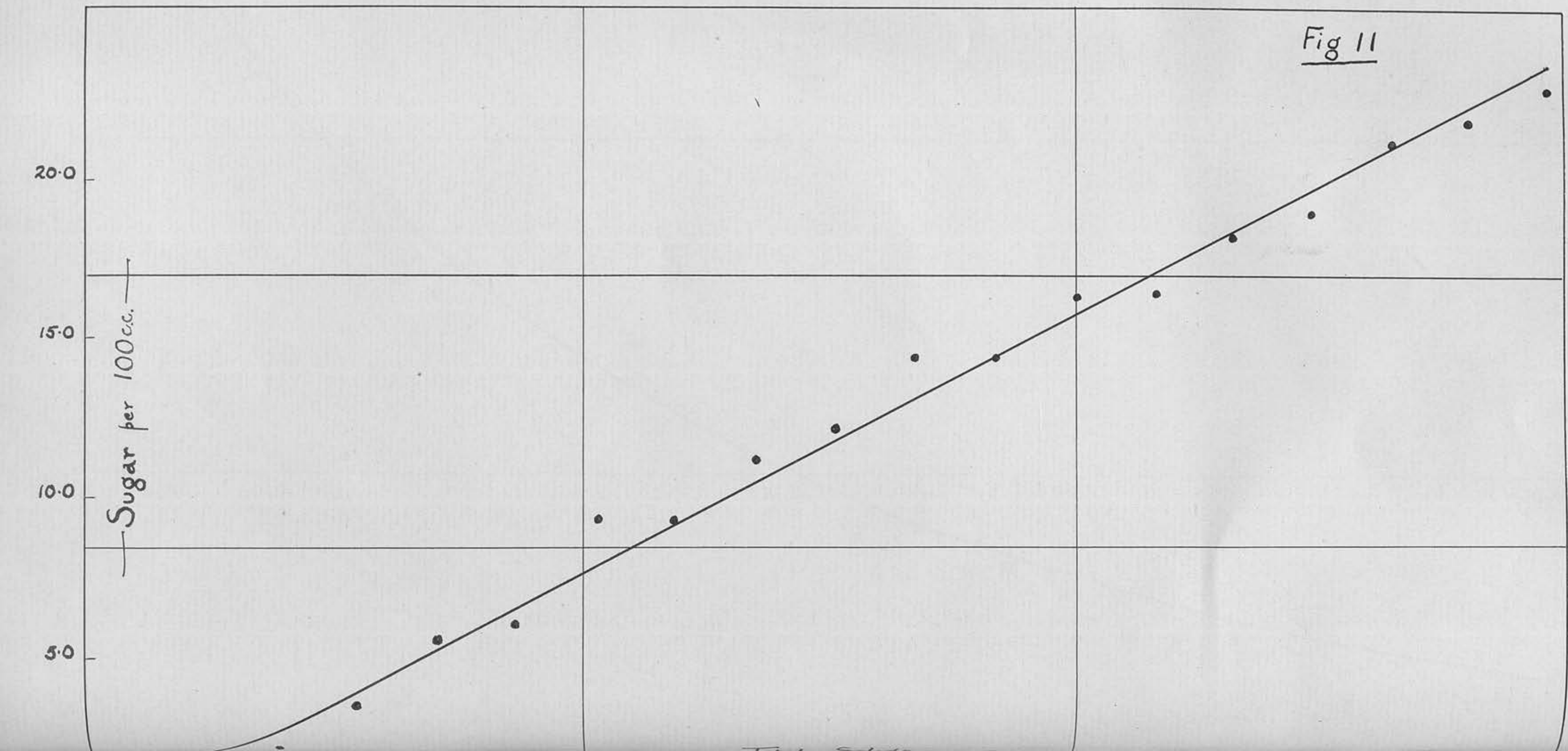
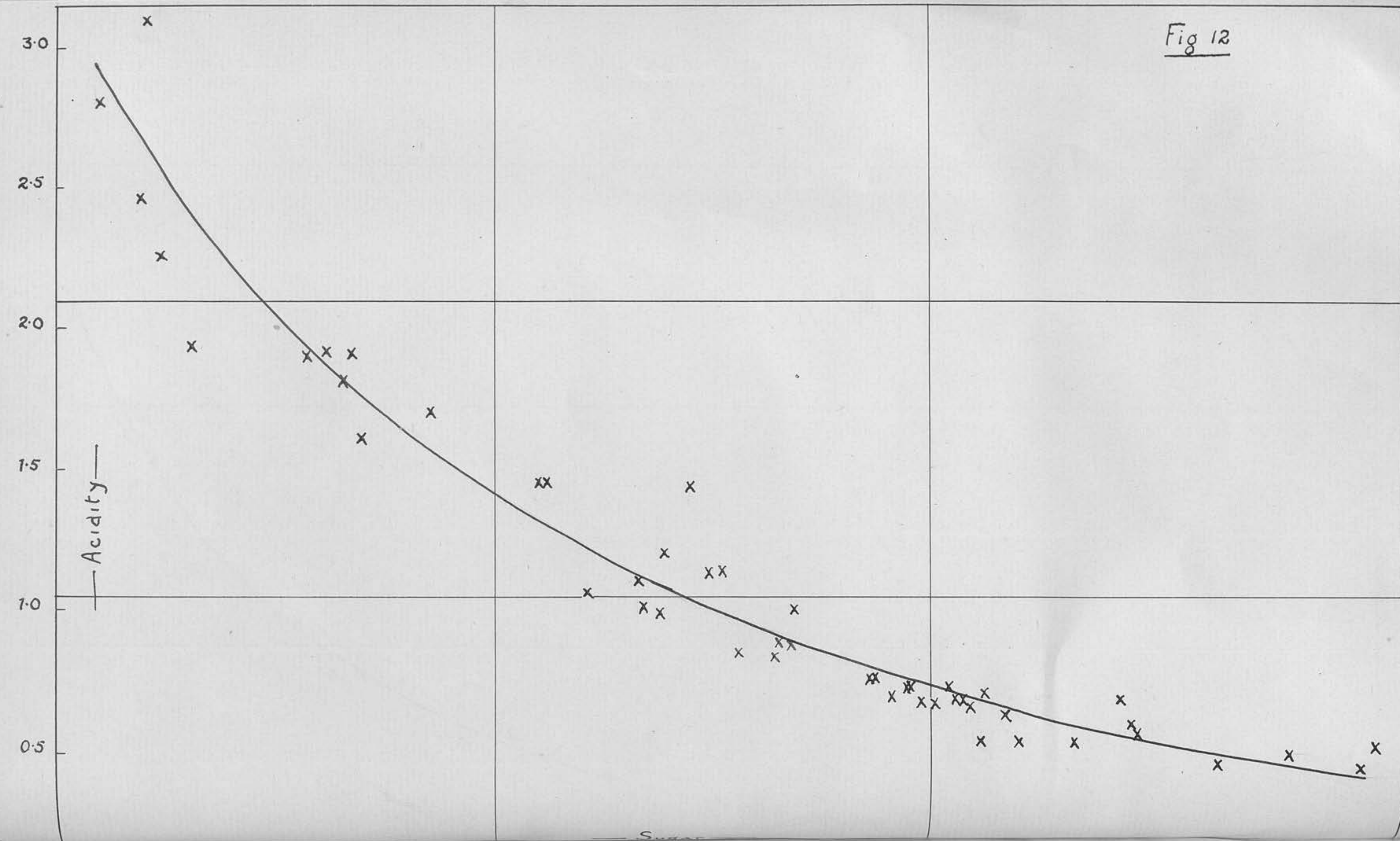


Fig 11
20·0
15·0
10·0
5·0
Sugar per 100 c.c.

Fig 12



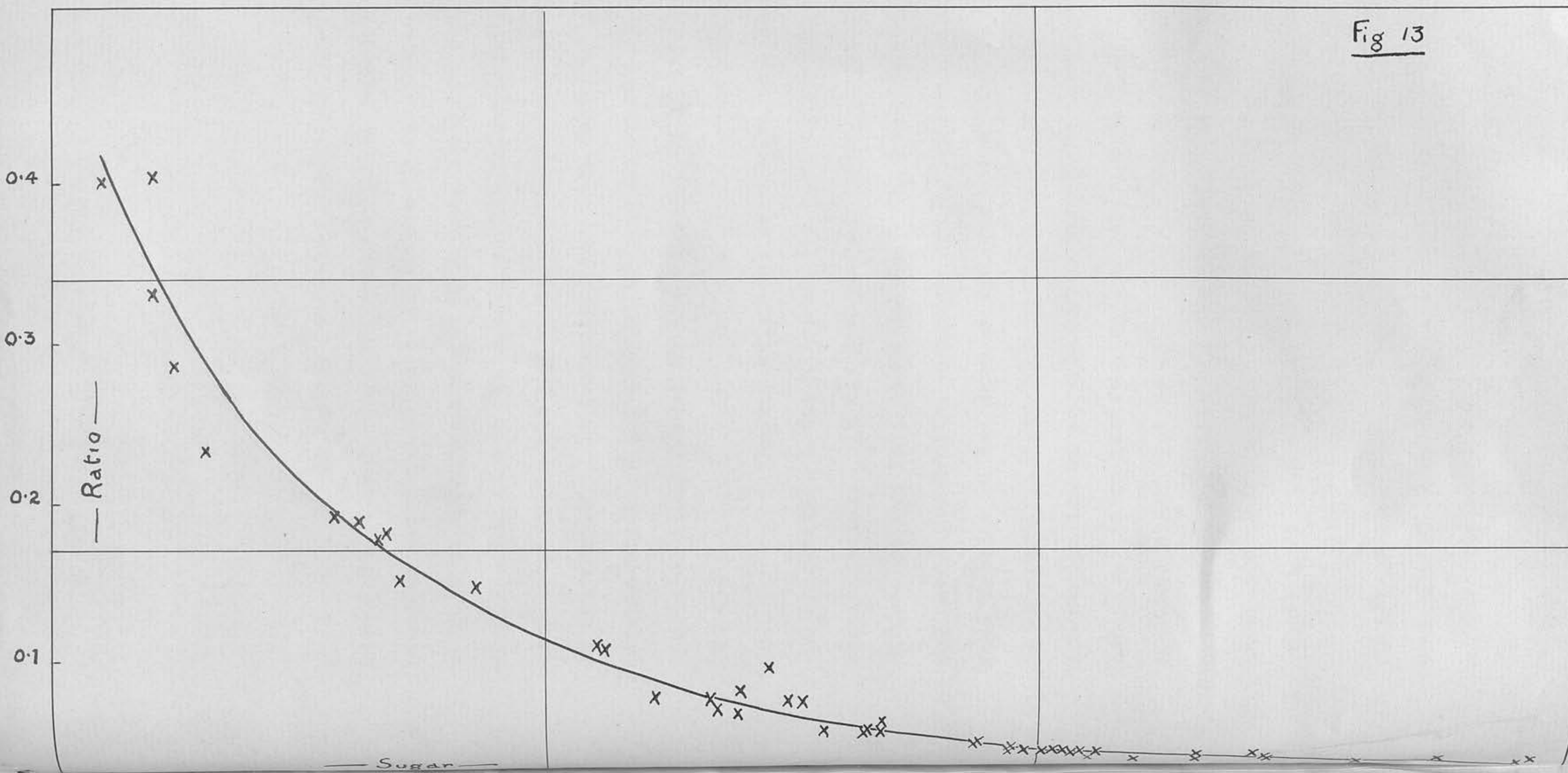


Fig 13

In course of publication by S.A. Assoc. for Adv. of Sc.

P.R.v.d.R.C.

SOME EFFECTS DUE TO THE SPRAYING OF FRUITS

BY

Th. Sect

P.R.v.d.R. Copeman, B.A., B.Sc.

In a paper * entitled "Chemical Investigations in regard to Citrus", Dr. Juritz has given an account of work that has been carried out in South Africa in connection with the effects of spraying oranges with lead arsenate for the purpose of combating insect pests such as the false codling moth. The results given in his paper confirm those obtained by workers † in California. It has been found that there is a marked deterioration in the flavour of sprayed fruits and this effect can be ascribed mainly to the decrease in acidity of sprayed fruits.

The investigation of oranges has been continued and in addition a few other fruits have been studied from this point of view. It has been stated ‡ that in general no consistent difference has been noted in the total sugar content of sprayed and unsprayed fruits, although Dr. Juritz has drawn attention to some results in the case of oranges which tend to show that there is apparently a reduction in the sugar content of sprayed fruits. The diminution of acidity is, however, the most striking and definite factor involved in the deterioration of flavour. The acid and sugar content of fruits are the most important factors governing the quality and the present paper deals only with these two quantities. In order to simplify the data the mean values have been employed for the purposes of comparison.

Since, in some cases, only a comparatively small number of analyses have been made it becomes necessary to have some method of estimating the significance to be attached to any differences which might be found to exist in the sugar and acid contents /

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* Dept. of Agric. Bull., Div. of Chem. Ser. No.60, 1925.
† Gray and Ryan, Mon. Bull. Dept. of Agric. Calif., 1921, 10, p.33.
‡ Gray and Ryan, loc. cit.

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contents of sprayed and unsprayed fruits. For this purpose a quantity known as "the standard error of the difference" has been calculated. If r_1, and r_2 be the standard errors of the two means separately, then the standard error of the difference will be $\sqrt{r_1^2 + r_2^2}$. The greater the number of samples employed the smaller will be the magnitude of the standard errors. Following the lead of Fisher,* the difference between two means is regarded as significant when it amounts to, at least, twice the standard error. Unless this condition be fulfilled then more than 5% of the values obtained may be outside the range of difference purely on account of random sampling. Naturally conditions other than the one under investigation must be under strict control.

The application of this method may be seen from the cases which are here reported. A consignment of sprayed and unsprayed Washington Navel oranges was received from an orchard in the Bathurst District. The unsprayed fruits were obtained from three rows of trees which had been left to act as controls. The spray used varied in strength from 1 oz. to $1\frac{1}{2}$ ozs. of lead arsenate in 4 gallons of water and was applied by means of a syringe so that a known amount of spray could be applied to each tree.

In Table I the results of analysis are given.

TABLE I.

ow.	"Units" of spray.	No. analysed.	Acid.	Difference. ± S.E.	Total Sugar per 100 c.c.	Sucrose / Total Sugar.	Difference. ± S.E.
A	0	18	1.438		8.27	.514	
B	567	6	.522	-.916 ±.075	8.86	.286	-.288 ± .037
C	378	9	.694	-.744 ±.058	8.90	.401	-.113 ± .031
D	231	9	.712	-.726 ±.110	8.36	.461	-.054 ± .018
E	Nicotine.	6	1.528	+.090 ±.069	7.87	.506	-.008 ± .017

The acid is expressed as grammes of citric acid per 100 c.c. of juice.

In /

* Fisher, "Statistical Methods for Research Workers". Oliver & Boyd, 1925.

In rows B, C, D, the term "units" of spray indicates the total amount of spray used for the trees in terms of the strength of the spray, amount at each treatment and the number of treatments. On examination of the table it will be seen that in every case the diminution of acidity is consistent and in all cases greater than twice the standard error. The decrease in acidity is therefore highly significant. The amount by which the acidity is decreased is apparently dependent upon the amount of spray used. It is clear that there is a definite reduction of acidity in sprayed oranges.

In the case of the total sugar it is found that the differences are not consistent and also that the differences have no significance and it may be concluded that the spraying does not definitely affect the total sugar content of the juice. In order to study the effect of the spray upon the relationship between the different sugars in the juice the ratio of sucrose to total sugar was employed. In all cases a significant diminution of this ratio was observed and it may be concluded that spraying with lead arsenate causes a definite disturbance in the equilibrium existing between the sucrose and invert sugar in the juice. It seems natural to assume that the sucrose becomes converted into invert sugar since the spraying has no significant effect upon the total sugar content.

In Dr. Juritz's paper mention is made of the fact that the sugar content of sprayed fruit is affected. In these cases the same methods as here employed indicate that in general the differences in total sugar content are not significant, but that the sucrose content of sprayed fruits is significantly smaller. Since the proportion of sucrose in normal oranges is practically 50% of the total sugar it may well be that the diminution of sucrose in sprayed oranges contributes in some way to the production of an insipid flavour in the fruit. On the whole it appears that the effect of the spray is more deeply seated than has hitherto been suspected. In a normal orange the flavour must depend upon some balance between the acid, sucrose and invert sugar in the juice and any change in this equilibrium must affect the flavour. In the present case the decrease of both acidity and sucrose leads to the development of the insipidity which is so marked a characteristic of sprayed oranges.

In order to determine whether this effect of spraying is confined to arsenical sprays a number of Washington Navel oranges sprayed with 40% Nicotine sulphate was obtained at the same time from the same orchard as the above specimens. The results of analysis are given in Row E of Table I where it can be seen that in none of the factors is there any significant difference. It may be concluded that the spraying in this case has no effect upon the fruit. As a matter of fact it has been found * that the deleterious effect is confined to arsenical sprays.

It is necessary that all the conditions, save the one under examination, be strictly controlled. Dr. Juritz has pointed out this difficulty in his paper in connection with a consignment of Valencia Late oranges. In the prsent case a consignment of Valencia Late oranges was received from the Bathurst District, but the sprayed and unsprayed fruits were from different orchards. The treated trees had been sprayed with poisoned bait by means of a syringe, about 72 units in all being employed. The bait was applied in the early part of the season and then baiting was discontinued. The results are given in Rows A and B of Table II in which the acid is expressed as in Table I.

TABLE II.

Row.	"Units" of spray.	No. analysed.	Acid.	Difference. ± S.E.	Total Sugar per 100 c.c.	Sucrose / Total Sugar.	Difference. ± S.E.
A	-	6	1.221		7.75	.474	
B	72	6	1.304	+.083 ± .081	7.83	.521	+.047 ± .018
C	-	8	1.836		7.11	.520	
D	+	6	1.237	-.599 ± .220	9.14	.455	-.065 ± .041

- unsprayed. + sprayed.

In /

* Gray and Ryan, loc. cit.

In this case it will be seen that the differences in acid and sucrose are positive and inconsistent with the facts already established. The difference in acidity between sprayed and unsprayed fruits increases as the season advances and apparently the comparatively small amount of spray used early in the season has not had the usually expected result, while the fruits themselves were apparently somewhat on the green side. Differences in the nature and position of the two orchards may account for this result. Dr. Juritz has stated that there is reason to believe that differences in type exist among Valencia Late oranges grown in the Bathurst District. Under these conditions it is clear that strict control is an absolute necessity, if correct conclusions are to be drawn.

The effect of the arsenate spray is not a transien one and may persist for a considerable period. In 1925 a consignment of valencia Late oranges was received from the Bathurst district and in this case the "sprayed" oranges were picked from trees that had been treated during the 1923-4 summer, but not during the 1924-5 summer. The results of analysis are given in Rows C and D of Table II.

In this case the fruits were of an uneven quality and it would seem that on further ripening the differences would be further accentuated. However, it is clear that the decrease in acidity is still highly significant. The effect of the treatment upon the proportion of sucrose is not so clearly defined but is nevertheless evident. It may be concluded that the effect of the spray persists for <u>at least</u> two seasons. It is apparent that the effect of spraying is general rather than local and that the absorption takes place through the leaves rather than through the rind of the fruit. The fact that all the oranges on tree are affected in the same way is also in accordance with this view.

To determine whether the deleterious action of the lead arsenate spray is confined to citrus fruits it was decided to carry out similar work in connection with other fruits In the first instance pears were chosen and three varieties were employed, namely, Beurre Hardy, Louise Bonne and Forelle. Consignments of the sprayed and unsprayed fruits of each variety were forwarded from Elsenburg. The spray, consisting of $1\frac{1}{4}$ lbs. of lead arsenate in 40 galls. of water, was used to combat codling moth. The sprayed fruit in the first two varieties were obtained from trees that had been treated five times and, in the last case, the trees were sprayed six times. The results obtained are summarised in Table III. In the case of the pears the acid is expressed as grammes of malic acid per 100 c.c., and the sugar in grammes per 100 c.c. of the juice.

TABLE III.

riety.	Treatment.	No. analysed.	Acid.	Difference ± S.E.	Total Sugars.	Sucrose. / Total Sugar.	Difference ± S.E.
urre Hardy	−	20	.160		13.27	.128	
Pears.	+	18	.109	−.051 ± .004	13.37	.128	—
uise Bonne	−	12	.151		11.81	.089	
Pears.	+	12	.130	−.021 ± .004	12.94	.109	+.020 ± .026
relle	−	24	.196		9.60	.279	
Pears.	+	24	.172	−.024 ± .013	10.55	.275	−.004 ± .021
ne Beauty	−	7	.651		9.66	.251	
Apples.	+	7	.436	−.215 ± .056	10.55	.445	+.194 ± .040

− unsprayed. + sprayed.

It will be seen that in all cases the effect of spraying is to cause a diminution of acidity while the effect upon the sugar is by no means significant. In this respect pears exhibit a distinct difference from oranges. On examining the data it will be seen that the percentage of acid in pears is very much less than in the case of oranges so that the actual magnitude of the difference in acidity due to spraying is very much smaller. At the same time the ratio of acid to sugar for pears is approximately 1 : 80 as compared with a value of about 1 : 12 for oranges, and the changes in this value due to the decrease in acidity are comparatively small in the case of pears as shown in Table IV. It will be seen that in the case of oranges the change in the ratio of acid to sugar is about 200% or more while the maximum change with pears is about 50%.

TABLE IV.

Ratio of Acid : Sugar.

	Unsprayed.	Sprayed.
Washington Navel Oranges.	5.6 5.1	17.0 13.0 11.7
Beurre Hardy Pears.	83.0	122.7
Louise Bonne.	78.3	99.5
Forelle.	50.0	61.3
Rome Beauty Apples.	15.0	24.9

At the same time in the case of pears the proportion of sucrose is about 13 - 25% of the total sugars compared with about 50% in the case of oranges. Under these circumstances it is hardly to be expected that the small diminution in acidity which does actually occur will affect the flavour of pears to the same extent as in the case of oranges. In point of fact no differences between sprayed and unsprayed pears can be detected by the palate. In practice, therefore, the effect of spraying pears with lead arsenate can be entirely ignored.

In order to study the effect of spraying with lead arsenate upon the flavour of apples a consignment of sprayed and unsprayed Rome Beauty Apples was received from Hankey in the Eastern Province. The sprayed trees were treated four times with a spray consisting of $1\frac{1}{4}$ lbs. in 40 galls. of water. The results of the analyses are given in Table III in which the acid is expressed as grammes of malic acid per 100 grammes and the sugar as grammes per 100 grammes of fruit.

In the case of the acidity the decrease in acidity is significant and it may be concluded that there is a definite diminution of acidity due to the spraying. There appears to be an effect upon the proportion of sucrose but when compared with the effect in the case of the other fruits this result seems to be somewhat inconsistent. As in the case of pears the magnitude of the acidity is comparatively small while the ratio of acid to sugar is approximately 1 : 20. The change in the ratio due to spraying is about 60%. Under these circumstances it is to be expected that any changes in the flavour of apples due to spraying will not be perceptible to the palate in the same way that the changes in the composition of pears cannot be detected. This conclusion is confirmed by the fact that no difference in taste can be detected between sprayed and unsprayed apples.

In general it would appear that the main factor involved in the spraying of fruit is the effect upon the acidity and that sprayed fruits have a lower acidity than unsprayed fruits. The flavour of a fruit seems to depend upon some equilibrium between the acid, sucrose and invert sugar in the juice. When this relationship is disturbed in the direction of diminished acidity and diminished proportion of sucrose the flavour of the fruit tends to become insipid.

In conclusion the author would like to express his thanks to Mr. Lounsbury for bringing this subject to his notice, to Dr. Pettey for kindly sending the samples from Elsenburg and to Mr. Gunn for his trouble in forwarding samples from the Eastern Province.

Th. Sect

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AN INVESTIGATION INTO THE COMPOSITION OF "WILDE DAGGA"

(*Leonotis leonurus* R.Br.)

BY

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(Read at a Meeting of the *Cape Chemical Society*, 15th September, 1922)

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An Investigation into the Composition of "Wilde Dagga."

(*Leonotis Leonurus* R.Br.)

By P. R. v. d. R. Copeman, B.A., B.Sc., Assistant Chemist, Division of Chemistry, Capetown.

(*Read at a Meeting of the Cape Chemical Society, 15th September,* 1922.)

The term "Dagga" is applied, somewhat indiscriminately, to several different plants, growing in South Africa. Of these plants, the one most widely known, owing to its evil reputation, is, in reality, Indian Hemp (*Cannabis indica*). This plant is frequently smoked by the natives, probably on account of the fact that, when the smoke is inhaled, powerfully intoxicating effects are produced. Investigations have been carried out on this plant by Wood, Spivey, and Easterfield.* From the resinous constituents they isolated a compound "cannabinol" to which they ascribed the poisonous properties of the plant. Another plant, namely, "Wilde Dagga," is reputed to possess similar properties, but this is an open question since a confusion of names certainly exists. However, for this reason it was thought that an examination of this plant (*Leonotis leonurus* R. Br.) might yield important results.

"Wilde Dagga" (*Leonotis leonurus*) is a labiate plant which grows in profusion in many parts of South Africa. It is a tall plant, about four feet high, with oblong serrated leaves. The plant may be easily recognized by the numerous whorls on its stem of light-red or orange coloured flowers. (See plate.) Its smell is strong and peculiar.

In Henslow's "South African Flowering Plants" it is stated that "the leaves are smoked by the natives; but, unlike Indian Hemp and tobacco, no member of the Labiates is poisonous . . . . but many secrete scented ethereal oils."† Dr. Marloth, in his presidential address to the Cape Chemical Society on "The Chemistry of South African Plants and Plant Products,"‡ states that *Leonotis leonurus* contains "some green resin which appears to be the cause of the narcotic properties, as well as some crystallizable substance."§ So far as is known this is the only reference to the chemical nature of the constituents of this plant.

A large number of references are made by different authorities to the medicinal properties of the plant. In Andrew Smith's "Contribution to South African Materia Medica" it is stated to be largely used in cases of snake-bite, colds, and tapeworm.|| In a paper on "Zulu Medicine and Medicine Men,"¶ the Rev. A. T. Bryant says: "To relieve the headache which is so generally an accompaniment of

* J. C. S. 1896, 79, 544. † *Op. cit.*, p. 214. ‡ May, 1913. § *Op. cit.* p. 13.
|| pp. 29, 103, 106. ¶ Annals of the Natal Govt. Museum, July 1909, p. 34.

these febrile attacks, a few leaves of the iMunyane (*Leonotis leonurus*) are pounded and steeped in cold water, and the liquid drawn into the nostrils." In the same paper a reference is made to the fact that the ground roots of this plant are mixed with those from other plants, and a hot infusion with water is made which is used in the treatment of snake-bite.* These facts indicate the possibility of a somewhat powerful drug being present, but nevertheless these statements seemed surprising in view of the fact that the Order (*Labiatae*) does not usually comprise plants containing substances with well-defined medicinal properties. On the other hand, information from natives themselves seems to point to the comparative harmlessness of the plant and to the fact that aqueous extracts are sometimes used as a lotion for open wounds.

Smith certainly *does* state† that extracts of the plant have an antiseptic action, while Dr. Gunn has informed the writer that the tincture acts as an anthelmintic. In this connection some remarks by T. A. Henry,‡ are interesting. He states that "most of the recent work on possible new anthelmintics has been devoted to the study of phenols. . . . Phenol, itself, is used as a remedy for thread worms, but it is too irritant for general use." Thymol is stated by him to be a valuable anthelmintic if its rate of absorption is not increased by mixture with oils, etc. It would seem, then, that phenolic compounds are valuable anthelmintics provided that their toxicity is not too great.

The present paper deals more particularly with the results of the examination of the aqueous extract, and confirms the existence of compounds with a possibly antiseptic and anthelmintic action. Two definite substances have been isolated, and they are both phenolic in character. At the same time, the quantities obtained did not permit of an investigation of their physiological properties. Dr. Gunn is at present engaged on this problem, and it is hoped that his results will shortly be published. The chemical results obtained up to date, however, are deemed of sufficient importance to warrant publication.

Experimental.

A proximate analysis of the leaves of the plant, which had been collected in the Malmesbury district, and allowed to become air-dry, was first made, according to the usual methods, with the following results:—

Moisture	9.51	per cent.
Ash	12.89	,,
Fats and waxes	10.51	,,
"Colouring matter"	2.60	,,
Soluble carbohydrates	11.74	,,
Soluble proteins	4.13	,,
Insoluble proteins	11.47	,,
Pentosans	13.02	,,
Fibre	12.06	,,
Insoluble carbohydrates (by difference)	12.07	,,
	100.00	,,

* *Ibid.* p. 73.

† Contrib. to S.A. Materia Medica. p. 45.

‡ "Some recent work on Anthelmintics" J.S.C.I. 1922, Nov. 15, 467, R.

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Moisture was determined by heating a weighed portion of the plant to 105° C. in a small watch-glass until a constant weight was obtained.

Ash was determined by igniting a weighed portion of the plant in a crucible until a constant weight was obtained.

Fats and waxes were determined by extracting with ether the dried original material or the dried residue from the determination of the "water-soluble" material. The ethereal extract was evaporated and the residue dried at 105° C.

"Colouring matter" includes the material extracted by alcohol after the moisture and water soluble and ether soluble constituents had been determined.

The "soluble protein" was determined by estimating the amount of nitrogen in the "water-soluble" residue and multiplying this by the factor 6.25.

The "soluble carbohydrates" include the amount of material soluble in water after deducting the "soluble protein" and the ash in the residue. The "water-soluble" material was estimated by digesting between 3 and 4 grammes of material with 150 c.c. of water, filtering and drying the residue at 105° C. The residue was then ignited and the weight of ash deducted.

"Insoluble proteins" were estimated by determining the "total nitrogen," multiplying this amount by 6.25, and then deducting the amount of "water-soluble" protein from the product.

Pentosans were obtained by distilling 2-4 grammes of the dried plant with 10 per cent. hydrochloric acid until 360 c.c. of distillate had been collected. By means of Fehling's solution the amount of furfural was determined in an aliquot portion of the distillate. This amount multiplied by the factor 1.710 gave the quantity of pentosan present.

Fibre was determined by the usual method, using 1.25 per cent. sulphuric acid and 1.25 per cent. caustic soda. 2-3 grammes were boiled under a reflux condenser for 30 minutes, with 200 c.c. of the reagents in turn. The residue was dried at 105° C. and then ignited. The weight of ash was deducted from the weight of dried residue.

The total amount of material extracted by alcohol was then determined by means of a Soxhlet.

Weight of air-dried leaves = 10.70 grammes.

Weight of extract, dried at 105° C. = 3.83 grammes.

Alcoholic extract = 35.8 percent. of the air-dried plant.

Water was then added to the alcoholic extract to precipitate the resinous material which was dried at 100° C. and weighed.

Resin = 19.8 per cent. of the air-dried plant.

20 grammes of the leaves were digested with a mixture of ammonia, ether, chloroform, and ethyl acetate, but the resulting extract gave no positive indication of the presence of any alkaloidal material in the plant.

For a complete examination, 3 kg. of the plant were extracted in four large Soxhlets with alcohol. Each Soxhlet was capable of holding 100 grammes, and each extraction was continued until the alcohol became colourless. The alcohol was then distilled off as completely as possible from the extract, and about 1 kg. of a thick viscid brownish-black residue was obtained. Water was added and the mixture steam-distilled for about 6 hours. The distillate was milky in appearance with a few drops of a clear yellow oil floating on the surface. The oil had a strong and persistent odour, somewhat resembling "old hay." The distillate, approximately 8 litres, was extracted with ether. A pale yellow solution was obtained, and this was evaporated to about 250 c.c. The ethereal solution was then extracted with 5 per cent. sodium carbonate solution, but this removed only a slight trace of an acid with an odour resembling closely that of valeric acid. The ethereal solution was then dried with anhydrous sodium sulphate and the ether finally distilled off. A clear reddish-yellow oil remained with a sweet fruity smell. The oil was then divided into three fractions by distillation.

Fraction I.—This fraction distilled between 75° and 83° C. (mostly 78-80° C.), and a colourless oil was obtained with a distinct odour of ethyl acetate.

$D_{20°} = .855$; $n_{22 \cdot 5°} = 1.3662$. Yield = 17.2 grammes.

Fraction II.—This distilled between 83° and 95° C. and was also a colourless oil with an odour of ethyl acetate, but it gave a slight furfural reaction.

$D_{20°} = .855$; $n_{23°} = 1.4174$. Yield = 4.8 grammes.

Fraction III.—This fraction distilled off between 128° and 234° C., with a rapid rise of temperature. It was a reddish oil with a penetrating odour, and gave a very strong furfural reaction.

$D_{20°} = .904$; $n_{24°} = 1.4554$. Yield = 1.5 gramme. Total yield of oil 23.0 grammes = .75 per cent. of the original plant.

The major portion of the first fraction is most likely ethyl alcohol judging from the constants given. This, of course, would be very likely owing to the fact that the alcohol used in the extraction was probably not completely driven off before steam-distilling. The true yield of oil then would be that contained in Fraction II and III, namely, 6.3 grammes.

There remained in the distillation flask a dark red aqueous liquid (A), and an insoluble brownish-black resinous product (B). When cold the two were separated and the resin thoroughly washed with warm water. The washings were then added to the liquid (A).

Examination of the Aqueous Liquid (A).

The liquid (A) was repeatedly extracted with ether until the ethereal solution was no longer coloured. The extract was then evaporated to small bulk, and extracted successively with ammonium carbonate, sodium carbonate, and caustic soda. In each case dark red solutions were obtained. On acidifying the first and third extracts, however, resinous products only were precipitated, and nothing crystalline could be isolated. The sodium carbonate extract on acidification with dilute sulphuric acid gave a yellow flocculent precipitate. This was filtered off, dissolved in alcohol, and water added to this solution until a faint turbidity appeared. On allowing the solution to cool a light yellow powder separated out. This darkened at about 150° C. and melted at 184-187° C. (uncorrected). With ferric chloride a dark green colouration resulted, but the amount isolated was too small to permit further investigation. From its manner of isolation it would appear to be some acid containing a phenolic group.

The original ethereal extract was then evaporated to a small volume. On standing this yielded a white residue of fatty appearance, On recrystallization from alcohol a small amount of a crystalline substance was formed; this softened at about 80° C. and finally melted at 168-178° C. The material was obviously impure, and it was therefore fractionally crystallized from alcohol when the least soluble fraction separated as a white flocculent powder which melted at 68-85° C. This was probably a mixture of fatty compounds. A middle fraction was obtained from the alcoholic solution, and it crystallized in small needles m.p. 233-234° C. (uncorrected).

Yield = .05 gramme.

It finally separated from a hot alcoholic solution in long needles when the solution cooled slowly. A determination of the molecular weight by Blackman's method* gave a value 203.

After the removal of the ether from the original aqueous liquid (A) by evaporation, the liquid (A) was extracted with chloroform, but this removed only a trace of a light yellow substance which could not be purified.

The aqueous liquid (A) was then freed from chloroform by steam-distillation, and, when cold, was thoroughly extracted with amyl alcohol, until the extract was no longer coloured. The extract was then concentrated on a water-bath by drawing a current of air over the surface of the liquid. The hot liquid, on cooling, deposited about .3 gramme of a yellow solid which was filtered off, and repeatedly crystallized from alcohol. Finally a pale yellow powder was obtained melting at 247-248° C. (uncorrected).

.2390 gramme of the substance, heated to 105° C., lost .0111 gramme,

whence H_2O = 4.65 per cent.

.0782 gramme on combustion gave .0389 gramme H_2O and .1558 gramme CO_2,

whence C = 54.34, H = 5.53.

No nitrogen could be detected in this compound.

$C_9H_{10}O_5$ requires C = 54.54, H = 5.05.

$C_9H_{10}O_5\ \frac{1}{2}H_2O$ requires H_2O = 4.34 per cent.

An acetyl derivative was prepared by boiling the substance with acetic anhydride and a drop or two of pyridine. On pouring the mixture into cold water a white crystalline product separated out, m.p. 126-127° C. (uncorrected).

.0283 gramme of this derivative gave .0130 gramme H_2O and .0566 gramme CO_2,

whence C = 54.54, H = 5.10.

Molecular weight by Blackman's method = 230.

$C_{11}H_{12}O_6$ requires C = 55.00, H = 5.00.

Molecular weight = 240.

Considering the small quantity of material available for combustion the figures for the combustion of the acetyl derivative are in good agreement and plainly indicate the presence of one hydroxyl group. The anhydrous compound must therefore have the constitution $C_9H_9O_4$ (OH).

The compound is only slightly soluble in water, but dissolves readily in alkalies forming a deep yellow solution. The addition of ferric chloride to a solution caused the appearance of a dark green colour. The compound showed reducing properties both with Fehling's solution and with ammoniacal silver nitrate. On the

* J. C. S. 1905, 87, 1474.

addition of lead acetate to an aqueous solution a yellow precipitate was formed. Concentrated sulphuric acid gave a faint greenish yellow colour.

From the amyl alcohol mother liquid whence this last product was obtained, only a very small amount of a yellow compound could be isolated, and on purification it proved to be identical with that previously obtained.

It was not found possible to identify this compound with any known substance, and it must therefore be regarded as a new compound.

The original aqueous liquid (A) was now freed from amyl alcohol by steam distillation, and basic lead acetate was added in two successive portions, so that the resulting precipitate was obtained in two fractions, both of which were well washed with water by decantation.

The first fraction of the precipitate was of a dirty green colour. It was suspended in hot water and decomposed by a current of sulphuretted hydrogen. The precipitate of lead sulphide was filtered off, and the clear reddish liquid was evaporated slowly to a thick syrup. This syrup was treated with alcohol until no more would dissolve. The alcoholic solution was concentrated to a small volume and poured into a large volume of ether when a dark red resinous material was precipitated. The clear ethereal liquid was decanted off and evaporated to a small volume. On allowing the liquid to stand in a desiccator for some time a pale yellow powder finally separated which was repeatedly crystallized from alcohol until the melting point remained constant at 229.5-230° C. (uncorrected).

(*a*) .1039 gramme on combustion yielded .0505 gramme H_2O and .1959 gramme CO_2,

(*b*) .0770 gramme on combustion yielded .0400 gramme H_2O and .1459 gramme CO_2,

whence (*a*) $C = 51.42$, $H = 5.40$.
whence (*b*) $C = 51.56$, $H = 5.64$.
$C_8H_{10}O_5$ requires $C = 51.63$, $H = 5.38$.

The substance was soluble in alkalies forming an orange-yellow solution, and its aqueous solution gave a dark green colouration with ferric chloride. This indicates the presence of at least one phenolic group. Concentrated sulphuric acid gave a bright lemon-yellow colour.

An acetyl derivative was prepared in the same way as in the previous case, and a flocculent gelatinous white mass was obtained. This was filtered off and well washed with hot water. The melting point was 135-136° C.

The composition and the reaction with ferric chloride indicate a close connection between this compound and that which resulted from the amyl alcohol extract. This compound, like the previous one, could not be identified with any known substance and must be regarded as a new compound; possibly it is an organic colouring matter of the type common in many plants.

The second fraction of the precipitate with basic lead acetate was pale yellow, and was produced by adding excess of basic lead acetate to the aqueous liquid (A). However, on treatment in the same way as the previous precipitate no crystalline material could be isolated.

The original aqueous liquid (A) was freed from lead and evaporated to a syrup. The liquid, however, showed only a very slight reducing action with Fehling's solution, and no osazone could be prepared.

There has, unfortunately, been very little opportunity of continuing the investigation by examining the material insoluble in water, but it is hoped to do so at a later date.

Summary.

A proximate analysis of the leaves of the plant "Wilde Dagga" (*Leonotis leonurus*) has been made.

An aqueous extract was prepared from the material soluble in alcohol by evaporating off the alcohol and adding water to the residue. The extract on steam-distillation yielded an oil of which the most important fraction was a reddish oil which had a high boiling point and showed a strong furfural reaction.

From the ethereal extract of the aqueous solution small quantities of a light yellow compound with m.p. 184-187° C., and with acid properties were isolated. This extract also yielded traces of a neutral substance of m.p. 233-234° C. and M.W. 203.

From the amyl alcohol a compound $C_9H_{10}O_5$ was isolated. It was shown to be phenolic in character and to possess one hydroxyl group. It crystallized with $\frac{1}{2}H_2O$ and melted at 247-248° C. An acetyl derivative was prepared and melted at 126-127° C.

By the use of lead acetate a second compound with the composition $C_8H_{10}O_5$ was isolated. This compound melted at 229.5-230° C. It was also phenolic in character and formed an acetyl derivative of m.p. 135-136° C.

These two compounds might possibly exert a slight antiseptic action, but they would not be likely to give rise to any powerfully intoxicating effects. On account of their phenolic character and slight solubility in water these compounds would probably exert a mild anthelmintic action such as extracts of the plant have been found to possess. Owing, probably, to the indiscriminate use of the term "Dagga" it is more than likely that erroneous assumptions have been made regarding the action of "Wilde Dagga."

In conclusion the author would like to state that this work was largely carried out in the laboratories of the University of Capetown. His thanks are due to Mr. S. K. van Niekerk for the supply of the large amount of material necessary for such work, and to Dr. Tietz for the interest he has shown in the progress of the work.

Th. Sect

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DEPARTMENT OF AGRICULTURE

(*Division of Chemistry Series No.* 31)

AN INVESTIGATION INTO SOME PHYSICAL AND CHEMICAL CHANGES OCCURRING IN GRAPES DURING RIPENING

By P. R. v. d. R. COPEMAN, B.A., B.Sc., D.Sc 1928
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By P. R. v. d. R. Copeman, B.A., B.Sc., Assistant Chemist, Division of Chemistry, Department of Agriculture.

During the grape season of 1922 the question of the ripeness of grapes arose in connection with their export. In South Africa, the regulations with regard to grapes stipulate that "no unripe grapes will be passed by the Inspector," but the general regulations provide that "all fruit shall be in sound condition, fully developed, and not too unripe." In America, a legal standard has been set up whereby the sugar-content of the juice must be at least 16-17 per cent. Balling scale, according to the variety of the grape.* This law was framed to prevent the indiscriminate shipment of green immature grapes, and it seems to have proved successful in practice.

In view of the indefinite nature of the terms "ripe" and "unripe" it is clear that any attempt to apply the regulations will be an entirely arbitrary proceeding, depending far too greatly on the personal factor. Individual discretion on these terms is bound to vary considerably. *What* constitutes a ripe grape? The condition of ripeness may be said to depend on the sense of taste. The seat of the sense of taste lies in the numerous papillae on the surface of the tongue, and the stimulation of these gustatory nerve endings by different substances gives rise to various sensations which may be broadly termed sweet, bitter, sour, and salt. Since sweetness is a desirable quality in fruit, attention is thus usually focussed upon the sugar-content, and, moreover, the flavour appears to be associated with the sugar-content. However, it is an important fact that the intensity of a sensation such as sweetness is considerably modified by the presence of an acid or sour substance.† Therefore, it may be concluded that the condition of ripeness will also depend on the acid-content. A high sugar-content and low acidity are desirable to give a mild sweet flavour.

At the present time there is no established method of determining when the grapes have reached a condition suitable for picking for export. The colour, firmness, and size all influence the picker's decision. A great many analyses of different varieties of grapes have been made both by American and by European investigators, but most of the analyses do not show the changes in composition during ripening. These changes have been studied, for American varieties, by Alwood‡ and his associates, by Bioletti, Cruess and Davis,§ and

* California Fruit and Vegetable Standardization Act, 1921.

† Zeitsch. f. Psych. u. Phys. der Sinnesorgane, 1899, Bd. 21.

‡ U.S. Bur. Chem. Bulls. 140, (1911); 145, (1911). U.S. Dept. Agr. Bulls. 335, (1916); 452, (1916).

§ Univ. of Cal. Pubs. in Agr. Sc., Vol. 3, No. 6, 1918.

by Noyes, King and Martsolf.* The European varieties have been studied by, amongst others, Brunel† and by Baragolia and Godet.‡ Lewis§ has published a paper dealing with the development of the grapes in South Africa, but his work dealt with those varieties of grapes which were suitable for wine-making, and the question was investigated mainly from this point of view.

The present paper is a description of some preliminary work undertaken to obtain an idea of the limits of some of the factors that influence the "condition of ripeness," in connection with table varieties of grapes, and the possibility of their export. It was also hoped that it would be possible to arrive at some definite numerical expression which would determine the stage at which a grape might be regarded as "ripe." Preferably, this test should be of a simple nature so that it could be applied by the average layman.

The work was carried out at the Government Wine Farm, Groot Constantia, during the period 31st January to 28th March, 1923. Four varieties of grapes were employed for the tests, namely, Red Hanepoot, White Hanepoot, Flaming Tokai, and Barbarossa, and determinations of different factors were made at definite intervals of a week until the exigencies of the vintage precluded further work. It was hoped that, by devoting as long a period as possible to this work, some definite idea would be obtained of the variations in the different factors.

In connection with the ripening of grapes it is clear, from what has been stated, that determinations of the sugar-content and acidity are essential. Therefore the density of the juice, expressed from the grapes, was determined both by the ordinary and by the Balling hydrometers. The amount of glucose, sucrose, and acidity was determined in the juice, and the hydrogen-ion concentration of the juice was ascertained. It is also obvious from the point of view of the picker that the average weight and average volume of the berries are important factors for determination. The volume of juice, obtainable from a given number of berries was also determined. It was, furthermore, decided to ascertain what change occurred in the amount of reduction shown by the juice with respect to potassium permanganate. Finally, since the amount of volatile matter present in the grape forms an important factor in the condition of the grape, the loss of weight on heating at 105° C. was determined. Conversely, this figure would also give the amount of total solids in the *berry*.

The rate at which the fruit develops naturally depends upon the climatic conditions. The season 1923 was remarkable for the small amount of rainfall, and in no case did rain interfere with the gathering and sampling of the grapes. Under these conditions, a high sugar-content and low acidity should be expected, and the results bear out this deduction.

Ten bunches of each variety of grape were collected in the early morning on one day each week during the period of the investigation. The whole sample was weighed, and from these ten bunches average samples of the berries were obtained. In making the determinations the methods employed were made as rapid as possible in order to

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* Journ. Assoc. Off. Agr. Chem., Vol. VI, No. 2, 1922.

† Rev. de Viticulture, Vol. 37, pp. 15–20.

‡ Landw. Jahr., Vol. 47 (1914), pp. 249–302.

§ Bull. Dept. Agr. 69, 1910.

obtain as many results as possible during the limited time available. This was also necessary in order to prevent errors due to changes occurring after the grapes had been picked and after the juice had been expressed from the berries.

The average weight was determined by weighing 100 berries which had been picked from all the bunches of the particular variety. In some cases this was done in duplicate and the result checked by the weights obtained in the "loss of weight" determinations.

The average volume was measured by determining the volume of water displaced by a convenient number of berries; in most cases the number was fifty. A 500 c.c. measuring cylinder was filled to 200 c.c. with water and the berries dropped in. The cylinder was well tapped to remove air-bubbles, and the increase in volume, as determined by the difference in the two readings, was taken as the volume of the berries.

The juice from 100 berries was pressed out by means of a masher with 1 mm. perforations. The juice was collected in a porcelain dish, filtered through coarse linen into a measuring cylinder, and the volume directly determined. The density of the juice was then taken by means of (*a*) an ordinary hydrometer, (*b*) a Balling hydrometer. Both these instruments contained a thermometer scale so that the temperature could be directly read. The readings were then corrected to 20° C. by means of tables.

The acidity was determined by diluting 10 c.c. of the filtered juice and titrating with N/10 alkali, using phenolphthalein as indicator. The result was calculated in terms of grams of tartaric acid per 100 c.c. of juice. The P_H value (hydrogen-ion concentration) was determined by comparing the colours obtained from the juice with a set of standard colours as published by Clark in "The Determination of Hydrogen Ions."

Glucose and sucrose were estimated by means of Benedict's method; 10 c.c. of juice was diluted slightly, clarified with 1 c.c. of lead acetate. The excess of lead was removed by means of sodium sulphate and the liquid made up to 250 c.c. The whole was then filtered, and the clear solution finally added slowly from a burette to 25 c.c. of Benedict's solution, which was kept at boiling point. The end-point was obtained when the solution became colourless. In the determination of sucrose, about 10 c.c. of hydrochloric acid was added before making up to 250 c.c. The clear filtered liquid was gently warmed for a short time to complete the inversion of the sucrose present. The amount of glucose and sucrose present were then calculated in grams per 100 c.c. of juice.

For the determination of the amount of reducing substances present in the juice, 10 c.c. was diluted to 250 c.c.; 10 c.c. of this solution was taken, excess of sulphuric added, the solution heated to boiling, and then titrated with N/10 potassium permanganate, until the faint pink coloration remained permanent. The results were calculated in terms of the number of cubic centimetres of N/10 permanganate used for 1 c.c. of pure juice.

The "loss of weight" was determined by heating ten berries at 105° C. until a constant weight was obtained. This loss represents water and volatile substances, and therefore the residue under these conditions represented the "total solids" in the berry. The results were calculated to 100 grams of the original berries.

The results of these analyses are collected in Tables I-IV.

Table I.

RED HANEPOOT.

Date.	Weight of 10 Bunches in grams.	Average Weight of a Berry in grams.	Average Volume of a Berry in c.c.	Volume of Juice in c.c. from 100 Berries.	Density of Juice at 20° C.	Balling at 20° C.	P_H of Juice	Acidity as Tartaric Acid.	Glucose.	Sucrose.	C.c. of $N/10 KMnO_4$ per 1 c c. of Juice.	% Loss of Weight.	% Total Solids in Berry.
								Grams per 100 c.c. of Grape Juice.					
31.1.23	2,037·0	4·11	3·83	178	1·0507	11·95	—	1·92	10·26	—	—	—	—
7.2.23	1,956·2	4·81	4·35	245	1·0695	16·62	2·8	·99	15·00	·37	—	—	—
14.2.23	2,891·7	5·25	4·77	265	1·0653	15·83	3·0	1·06	13·93	·32	—	88·21	11·8
21.2.23	3,614·7	5·95	5·80	340	1·0753	17·81	3·0	·87	16·81	·27	96·17	86·65	13·4
1.3.23	3,670·0	6·15	5·60	315	1·0780	18·30	3·4	·70	18·28	·43	95·8	82·15	17·8
7.3.23	4,790·0	6·40	6·10	325	1·0830	20·10	3·6	·54	19·50	·50	113·6	81·54	18·5
14.3.23	4,445·0	6·45	5·80	355	1·0859	20·44	3·8	·54	20·01	1·08	111·8	84·93	15·1
21.3.23	2,905·0	6·40	6·18	325	1·1001	23·50	4·0	·45	22·89	1·32	124·8	81·95	18·1
28.3.23	3,670·0	5·22	4·60	293	1·1047	23·94	4·1	·44	24·94	2·15	144·4	77·18	22·8

Table 11.

White Hanepoot.

Date.	Weight of 10 Bunches in grams.	Average Weight of a Berry in grams.	Average Volume of a Berry in c.c.	Volume of Juice in c.c. from 100 Berries.	Density of Juice at 20° C.	Balling at 20° C.	P_H of Juice.	Acidity as Tartaric Acid.	Glucose.	Sucrose.	C.c. of $N/10 KMnO_4$ per 1 c.c. of Juice.	% Loss of Weight.	% Total Solids in Berry.
								Grams per 100 c.c. of Grape Juice.					
7.2.23	2,256·8	4·11	3·80	188	1·0658	15·67	3·0	1·44	15·40	—	—	—	—
14.2.23	2,806·7	4·96	4·80	228	1·0678	16·12	3·4	1·14	15·86	·11	95·7	85·96	16·0
21.2.23	4,324·4	5·22	4·70	280	1·0684	16·58	3·4	·85	16·09	·24	94·2	80·84	19·2
1.3.23	3,299·0	5·40	5·18	242	1·0807	18·05	3·6	·69	18·68	·39	95·9	80·07	20·0
7.3.23	5,103·0	5·93	6·00	327	1·0793	18·24	3·8	·68	19·38	·30	108·9	83·50	16·5
14.3.23	4,149·0	5·98	5·75	300	1·0909	20·86	3·9	·56	21·75	·66	117·2	82·45	17·5
21.3.23	2,941·0	5·72	5·06	302	1·1023	23·66	4·0	·49	23·91	·97	121·4	81·01	19·0
28.3.23	2,551·0	5·20	5·03	225	1·1070	24·20	4·0	·52	25·16	1·46	124·8	82·11	17·9

Table III.

FLAMING TOKAI.

Date.	Weight of 10 Bunches in grams.	Average Weight of a Berry in grams.	Average Volume of a Berry in c.c.	Volume of Juice in c.c. from 100 Berries.	Density of Juice at 20° C.	Balling at 20° C.	P_H of Juice.	Acidity as Tartaric Acid.	Glucose.	Sucrose.	C.c. of $N/10\,KMnO_4$ per 1 c.c. of Juice.	% Loss of Weight.	% Total Solids in Berry.
								Grams per 100 c.c. of Grape Juice.					
7.2.23	2,835·0	4·96	4·90	262	1·0576	14·12	3·2	1·56	11·94	—	—	—	—
14.2.23	1,601·8	4·51	4·10	220	1·0614	15·57	3·3	1·29	14·63	·03	85·3	85·31	14·7
21.2.23	3,614·7	5·80	5·75	287	1·0580	14·64	3·4	1·21	13·60	·13	86·2	83·01	17·0
1.3.23	3,322·0	6·12	5·75	303	1·0660	15·80	3·4	·94	14·03	·37	84·4	84·56	15·4
7.3.23	4,962·0	6·31	6·83	300	1·0833	19·86	3·6	·70	19·34	·65	118·9	83·44	17·6
14.3.23	4,390·0	6·35	7·00	382	1·0779	19·00	3·8	·62	19·26	·67	116·8	83·45	17·5
21.3.23	2,808·0	6·33	5·90	340	1·0803	18·66	3·9	·60	19·29	·84	113·1	85·63	14·4
28.3.23	1,951·0	6·11	5·98	342	1·0860	20·14	4·0	·44	20·53	1·72	119·0	81·72	18·3

Table IV.

BARBAROSSA.

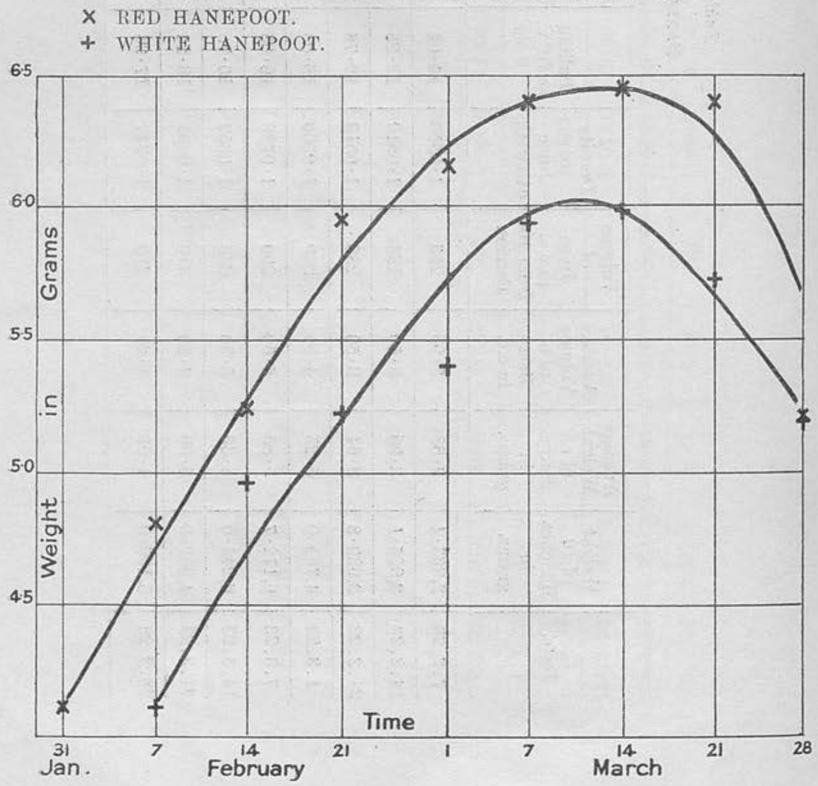
Date.	Weight of 10 Bunches in grams.	Average Weight of a Berry in grams.	Average Volume of a Berry in c.c.	Volume of Juice in c.c. from 100 Berries.	Density of Juice at 20° C.	Balling at 20° C.	P_H of Juice.	Acidity as Tartaric Acid. (Grams per 100 c.c. of Grape Juice.)	Glucose. (Grams per 100 c.c. of Grape Juice.)	Sucrose. (Grams per 100 c.c. of Grape Juice.)	C.c. of $N/10\,KMnO_4$ per 1 c.c. of Juice.	% Loss of Weight.	% Total Solids in Berry.
7.2.23	2,863·4	3·68	3·90	235	1·0555	14·02	3·2	1·25	12·50	—	—	—	—
14.2.23	3,005·1	3·90	3·50	195	1·0510	12·26	3·4	1·24	10·96	·27	—	89·45	10·6
21.2.23	3,629·8	3·64	3·50	230	1·0513	12·76	3·4	·93	11·33	·09	77·8	83·48	16·5
1.3.23	4,785·0	5·25	4·90	290	1·0660	16·00	3·6	·75	13·29	·12	77·2	84·06	16·0
7.3.23	6,172·7	5·85	5·60	290	1·0780	19·06	3·8	·66	17·20	·20	87·8	86·78	13·2
14.3.23	6,245·0	5·66	5·38	335	1·0659	16·75	3·8	·61	16·24	·34	91·2	88·08	11·9
21.3.23	4,960·0	5·00	4·80	310	1·0691	16·26	3·9	·47	16·52	·78	101·5	86·51	13·5
28.3.23	5,190·0	4·62	4·20	210	1·0747	17·94	4·0	·45	18·86	1·34	113·3	85·40	14·6

Of these data, the most important are those for sugar-content and acidity. These quantities are the most easily determined, and the quality of the grape will depend most largely on them. Owing to the difficulty of obtaining really representative samples from a product so widely variable as a fruit, there is naturally a certain amount of irregularity in the analyses at different dates. Nevertheless, the tendency for the percentage of sugar to increase as the season advances is clear from the tables. At the same time the percentage of acid decreases as the fruit becomes mature, and this, at least, is partly responsible for the decreased astringency of the fruit. However, the two changes were not directly proportional to one another.

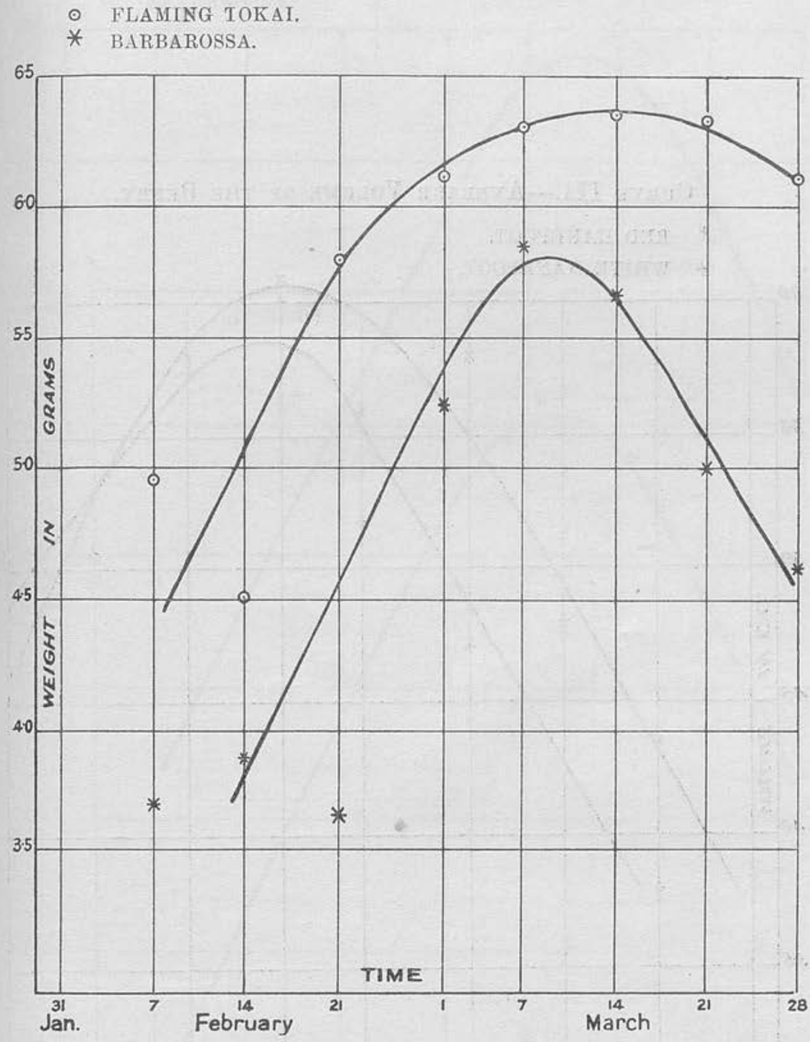
In order to present the data in a manner in which they may be readily studied, the results have also been presented in the form of curves. On account of the difficulty, already mentioned, of obtaining really representative samples, the analytical data could not be expected to fall completely on any given curve. However, in order to simplify them, the curves have been smoothed out and irregularities regarded as experimental errors. The curves, so obtained, probably represent with some degree of accuracy the changes occurring during the ripening of the grapes.

One fact of remarkable interest was made clear in these curves. It was found that the curves formed two series, namely:—Series A, in which the curves for Red Hanepoot resembled very closely those for White Hanepoot, and Series B, in which the curves for Flaming Tokai and Barbarossa resembled one another. These facts are most clearly evident in the curves for density, balling, and glucose, and the close resemblance between Red Hanepoot and White Hanepoot was spcially significant.

Curve Ia.—Average Weight of Berries.



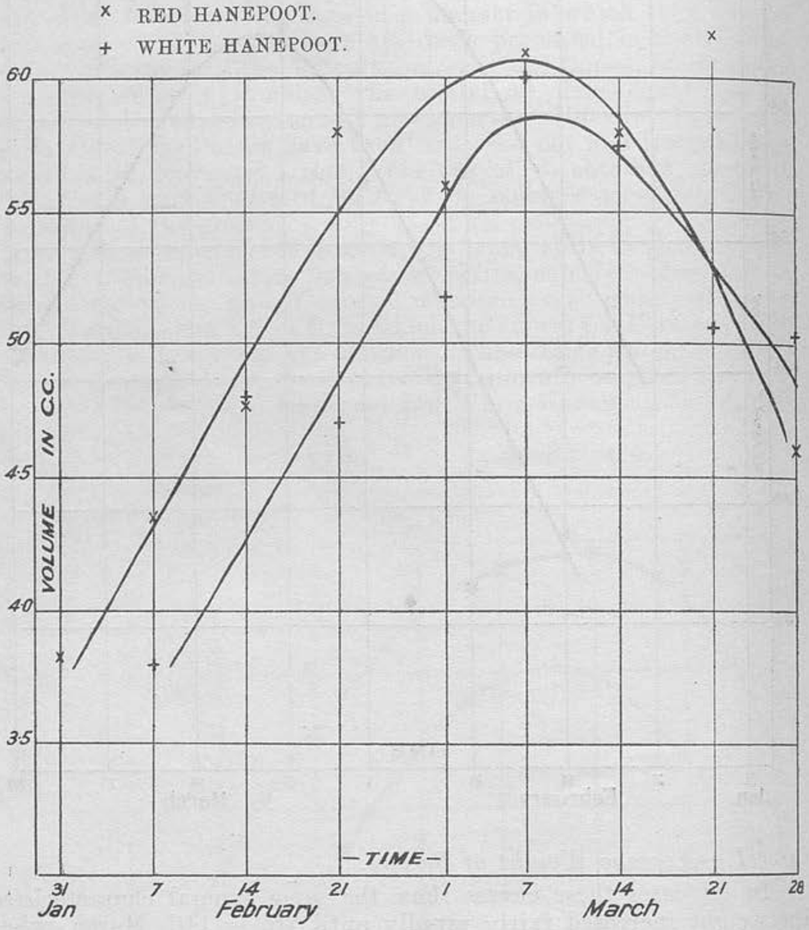
Curve Ib.—Average Weight of Berries.



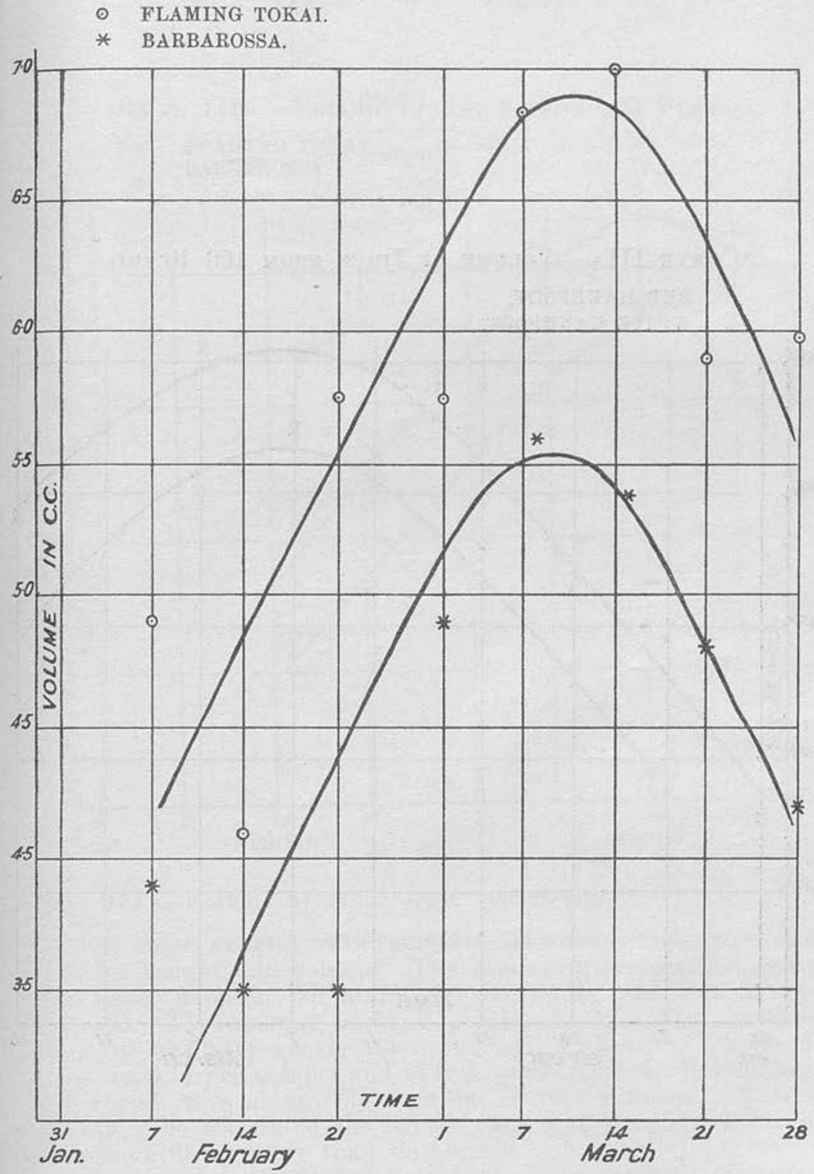
Curve I.—Average Weight of Berries.

In all cases these curves show the same general characteristcs. The weight increased fairly rapidly until 7th to 14th March, when this factor reached its maximum value. With the Barbarossa variety, this point of maximum weight was slightly earlier, and, in the case of Flaming Tokai, slightly later than with the two Hanepoot varieties. At this point the berry had reached its fullest development, and after this the weight decreased. Owing to the firm nature of the Flaming Tokai berry, this decrease was not as evident as with the softer varieties. It may be supposed that the berry is gradually cut off from the influence of the growing processes in the plant, and begins to lose weight owing to the loss of volatile matter from the berry.

Curve IIa.—Average Volume of the Berry.



Curve IIb.—Average Volume of the Berry.

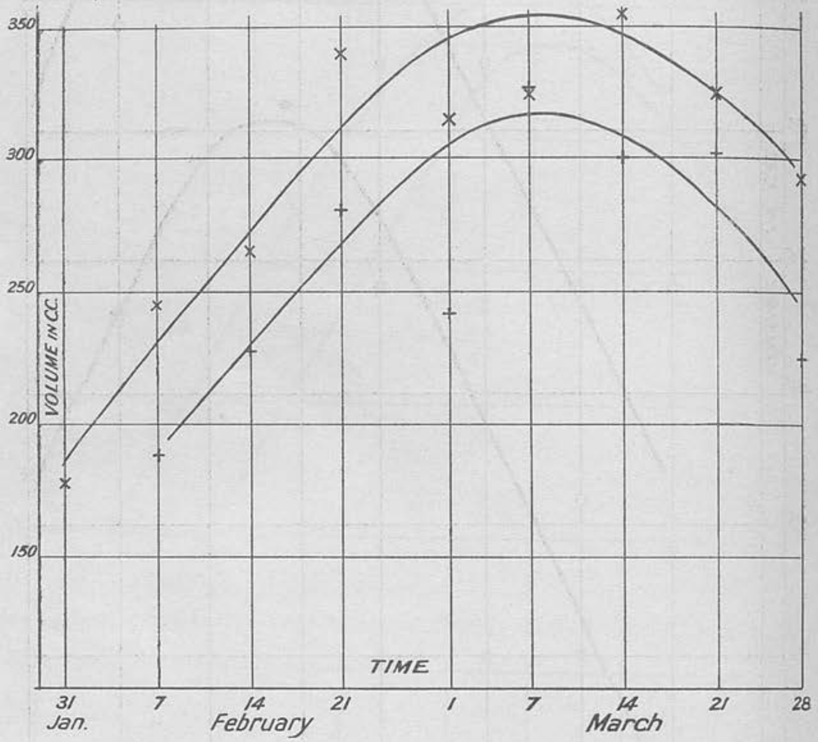


Curve II.—Average Volume of the Berry.

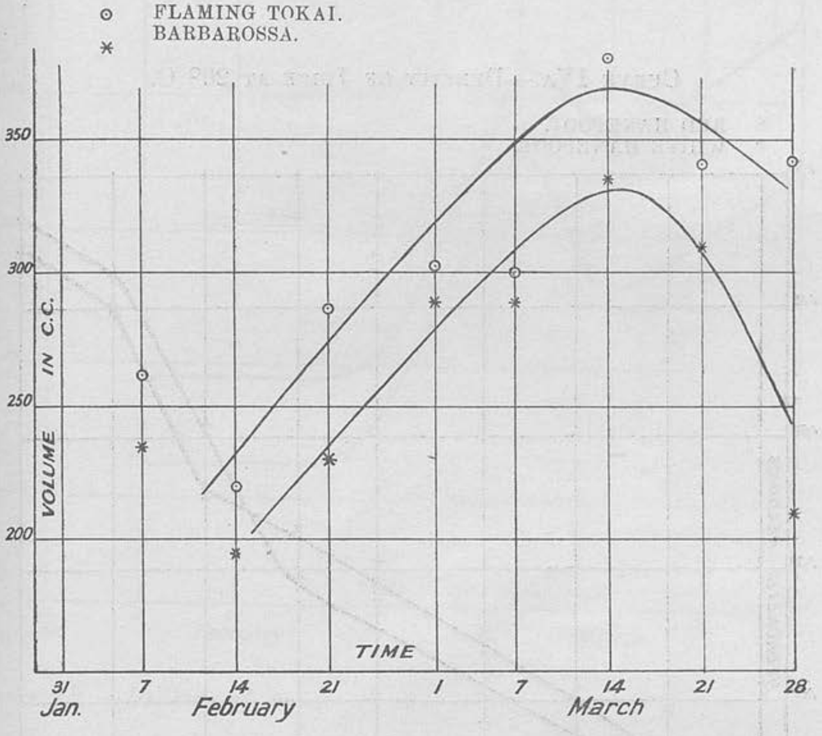
The volume changes followed closely the changes of weight in the berry, and the maximum volume was attained about the 7th March, although this point was only reached a few days later by the Flaming Tokai. After this stage had been reached the volume diminished and the grapes began to shrink. These changes are probably due to the same cause as that to which the decrease in weight is ascribed.

Curve IIIa.—Volume of Juice from 100 Berries.

× RED HANEPOOT.
+ WHITE HANEPOOT.



Curve IIIb.—Volume of Juice from 100 Berries.

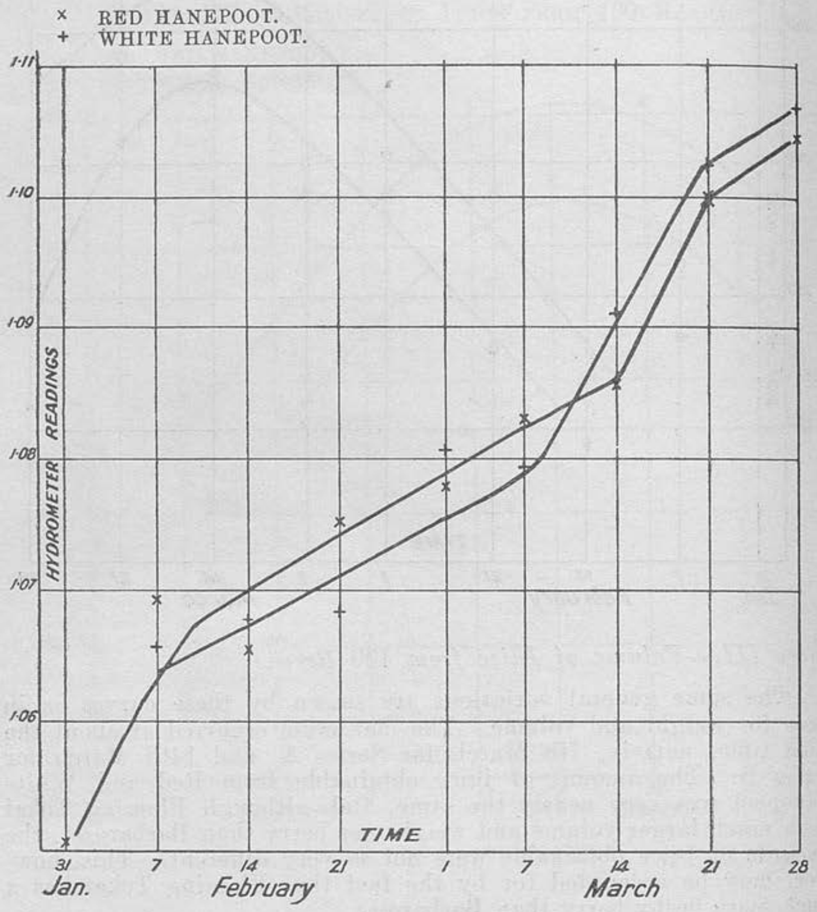


Curve III.—Volume of Juice from 100 *Berries.*

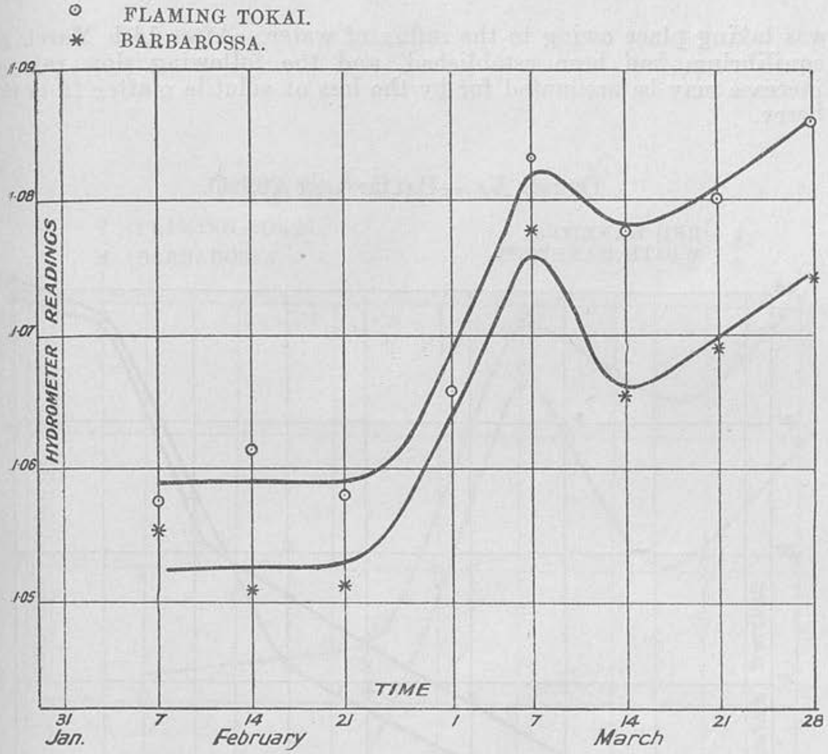
The same general variations are shown by these curves as in those for weight and volume. The maximum occurred at about the same time, namely, 7th March for Series A, and 14th March for Series B. The amount of juice obtainable from Red and White Hanepoot was very nearly the same, and, although Flaming Tokai has a much larger volume and weight per berry than Barbarossa, the amounts of juice obtainable were not so very different. This, however, may be accounted for by the fact that Flaming Tokai has a much more fleshy berry than Barbarossa.

If these three factors alone were to be considered, the period of fullest development would be fixed at about 7th March, when all three factors were at, or very close to, their maximum value. At this stage, then, the grapes would be regarded as "ripe."

Curve IVa.—Density of Juice at 20° C.



CURVE IVB.—DENSITY OF JUICE AT 20° C.

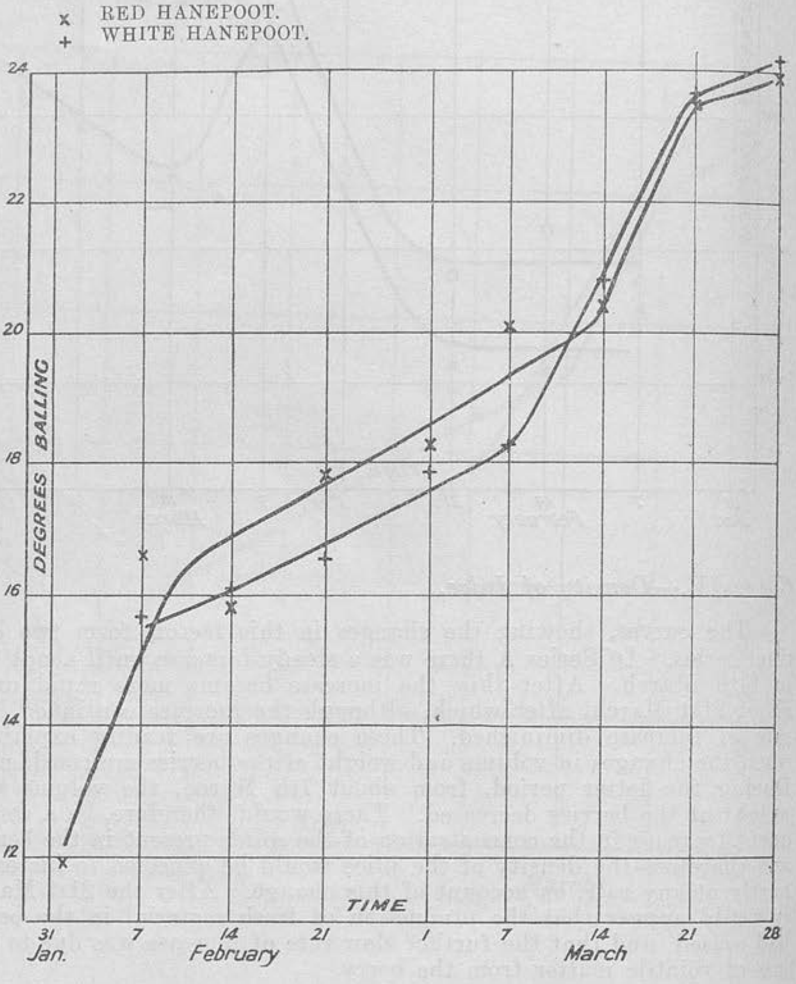


Curve IV.—Density of Juice.

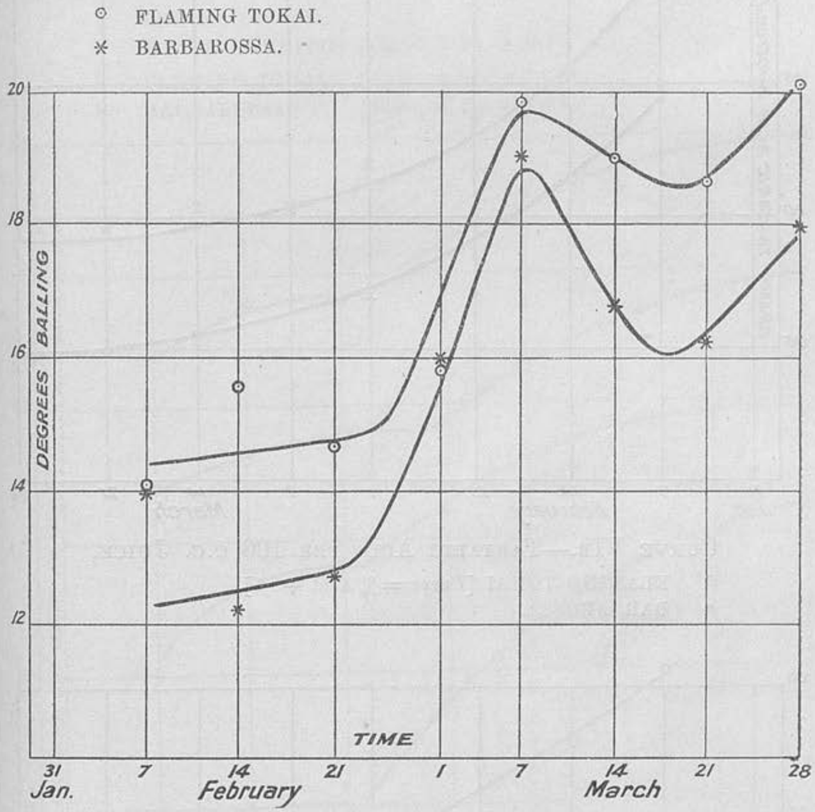
The curves, showing the changes in this factor, form two distinct series. In Series A there was a steady increase until about 7th to 14th March. After this, the increase became more rapid until about 21st March, after which, although the increase continued, the rate of increase diminished. These changes are readily explained when the changes in volume and weight of the berries are considered. During the latter period, from about 7th March, the volume and weight of the berries decreased. There would, therefore, be a consequent increase in the concentration of the solids present in the berry, and therefore the density of the juice would be expected to increase, partly at any rate, on account of this change. After the 21st March it would appear that the production of fresh material in the berry had ceased, and that the further slow rate of increase was due to the loss of volatile matter from the berry.

In Series B there seemed to be a tendency for the density of the juice to remain fairly constant until about 21st February, after which there was a sudden increase until about 7th March. This would be due to a rapid concentration of solids in the berry during the process of ripening. From 7th March to 14th March there was a slight decrease in the concentration of solids, probably owing to the fact that a maximum of solids had been attained and that slight dilution was taking place owing to the influx of water. After 14th March an equilibrium had been established, and the following slow rate of increase may be accounted for by the loss of volatile matter from the berry.

Curve Va.—Balling at 20° C.



Curve Vb.—Balling at 20° C.



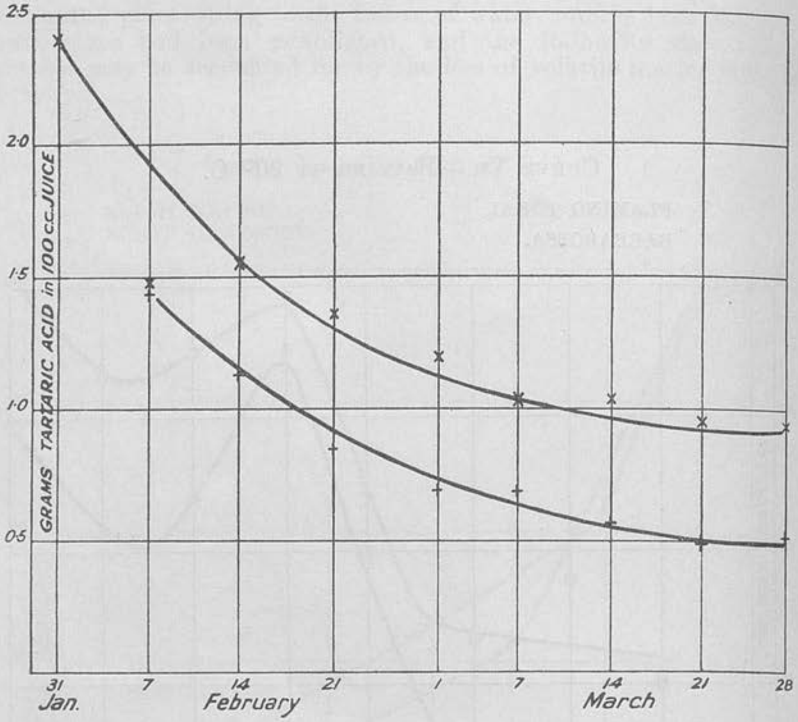
Curve V.—Degrees Balling of the Juice.

These curves show the same general characteristics as the curves for density. This was to be expected from the nature of the determination, and the explanation of the various changes would be the same.

CURVE VIA.—GRAMS TARTARIC ACID PER 100 C.C. JUICE.

× RED HANEPOOT [Curve = % Acid + ·5].

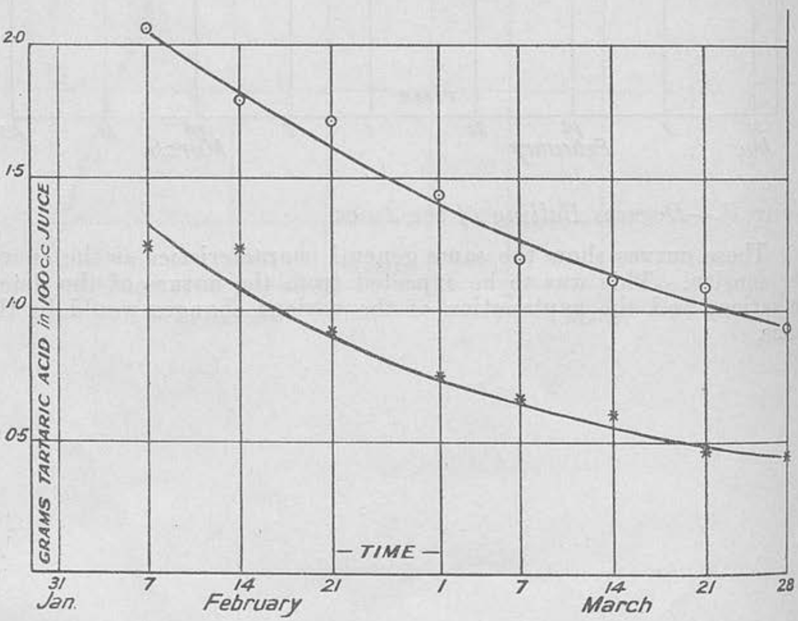
+ WHITE HANEPOOT.



CURVE VIB.—TARTARIC ACID PER 100 C.C. JUICE.

⊙ FLAMING TOKAI [Curve = % Acid + ·5].

* BARBAROSSA.

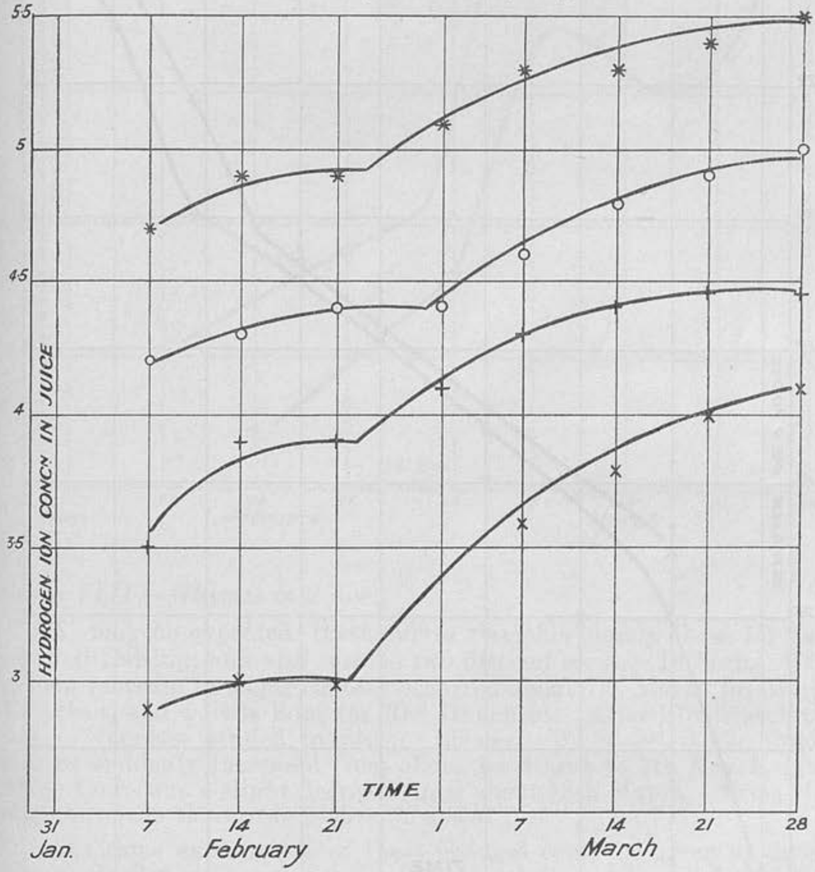


Curve VI.—Acidity as Tartaric Acid.

These curves show that there was a gradual and continuous decrease of acidity throughout the whole season. In Series A this factor tended to reach a limiting value, namely, about 0.5 per cent. of tartaric acid for both varieties of Hanepoot. The decrease of acidity was not so marked as the increase in sugar-content.

CURVE VII.—HYDROGEN-ION CONCENTRATION IN JUICE.

× RED HANEPOOT.
+ WHITE HANEPOOT [Curve = Ph. + 0·5].
○ FLAMING TOKAI [Curve = Ph. + 1·0].
✳ BARBAROSSA [Curve = Ph. + 1·5].



Curve VII.—Hydrogen-Ion Concentration of the Juice.

There was an increase in this value throughout the whole season, although in the case of White Hanepoot and Barbarossa it tended to reach a limiting value of 4.0. In every case there was a change in the rate of increase. In White Hanepoot, Red Hanepoot, and Barbarossa this change occurred shortly after 21st February, and in Flaming

Tokai less than a week later. In Red Hanepoot and Flaming Tokai there was a more rapid decrease of free acid than in the two other varieties.

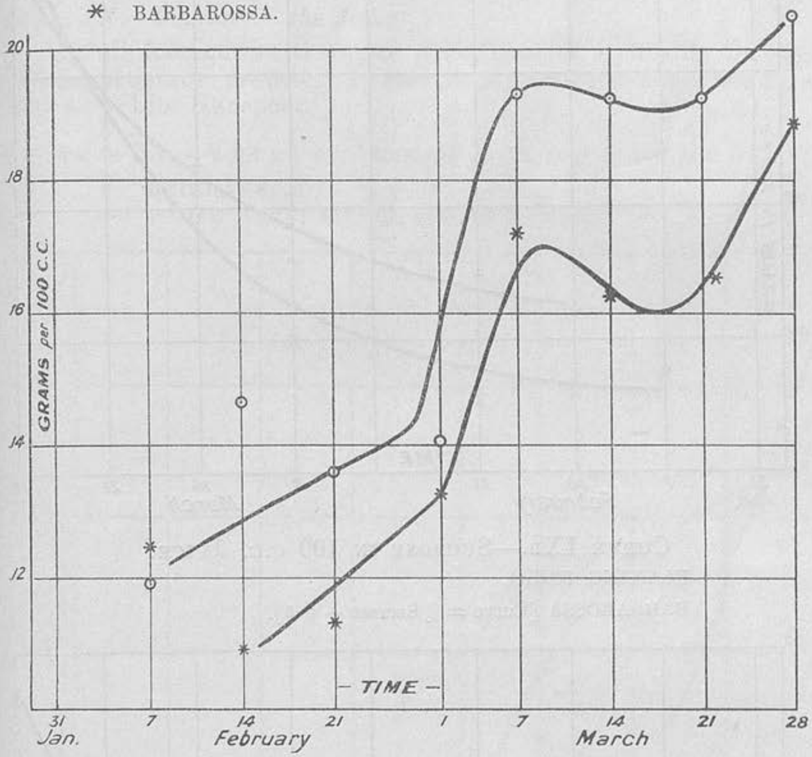
Curve VIIIa.—Glucose in 100 c.c. Juice.

× RED HANEPOOT.
+ WHITE HANEPOOT.

Curve VIIIb.—Glucose in 100 c.c. Juice.

○ FLAMING TOKAI.

* BARBAROSSA.



Curve VIII.—Glucose in Juice.

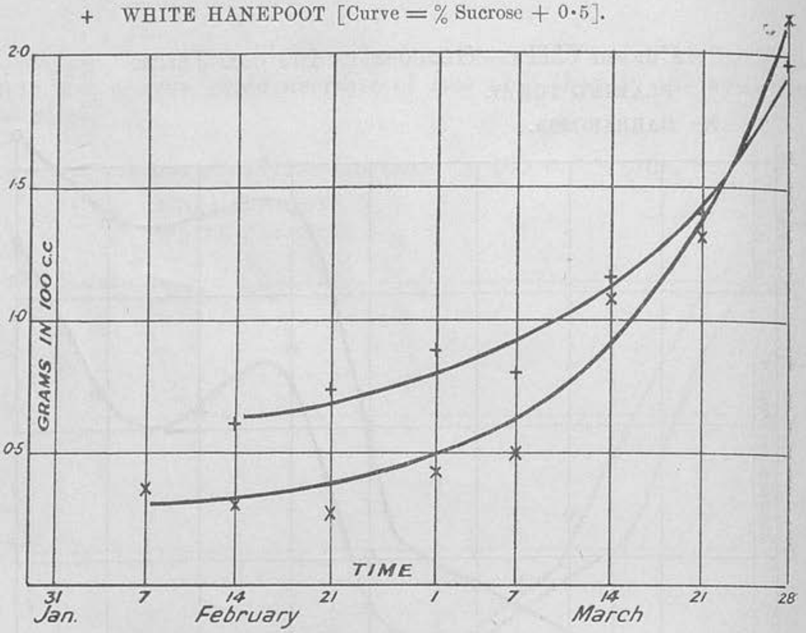
As may be expected, these curves resemble closely those for density and Balling, and also formed two distinct series. In Series A the sudden increase in sugar-content occurred about 7th March for White Hanepoot, and a little later for Red Hanepoot. After 21st March the rate of increase tended to become slower. In Series B the sugar-content suddenly increased from about 1st March to 7th March, after which there was a slight decrease until about 18th March. From this stage onwards there was a slow increase.

The same explanation of these changes could be given as in the case of the density curve. After 21st March it may be concluded that no further production of glucose occurred, and any further increase in sweetness of the grapes would be mainly due to a decrease in the amount of free acid present in the berry.

Curve IXa.—Sucrose in 100 c.c. Juice.

x RED HANEPOOT.

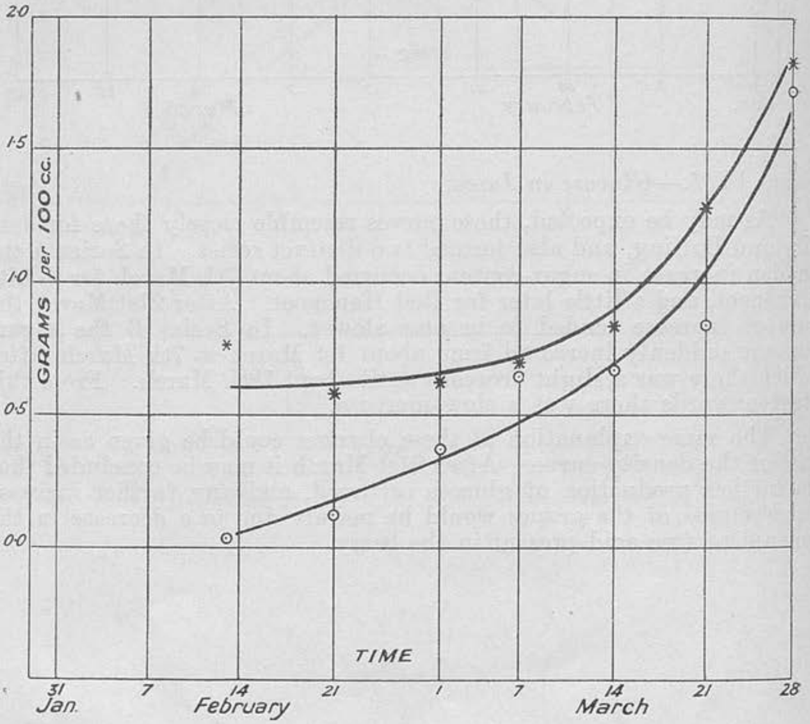
+ WHITE HANEPOOT [Curve = % Sucrose + 0·5].



Curve IXb.—Sucrose in 100 c.c. Juice.

○ FLAMING TOKAI.

✳ BARBAROSSA [Curve = % Sucrose + 0·5].



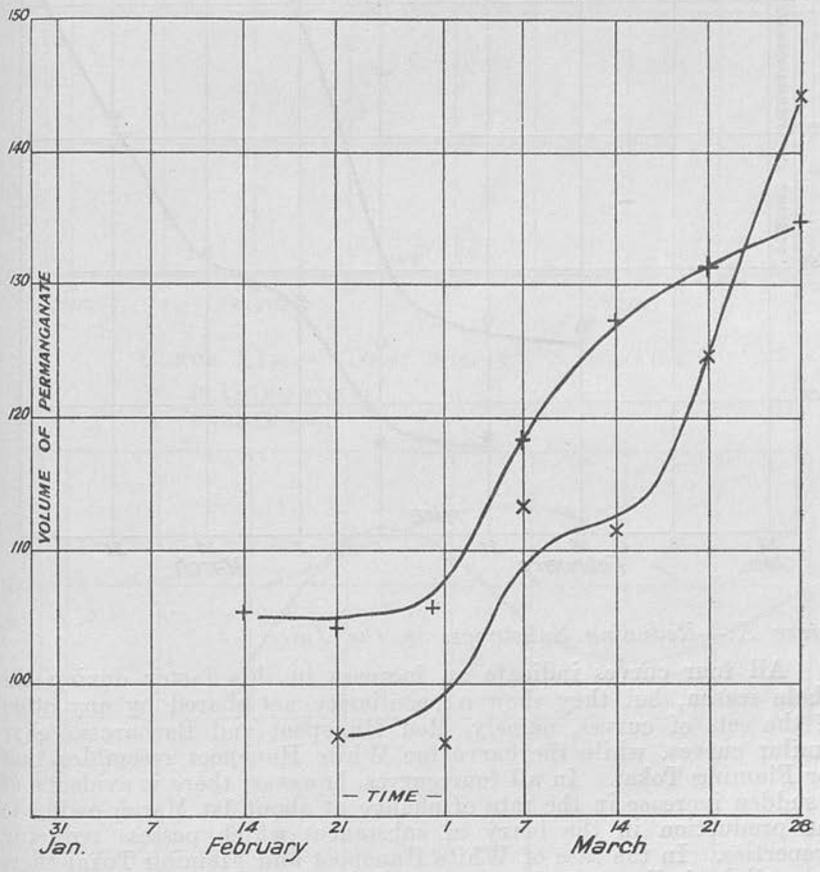
Curve IX.—Sucrose in the Juice.

In all four curves there are indications of a steadily increasing amount of sucrose present. In Red Hanepoot the increase was greater than in White Hanepoot.

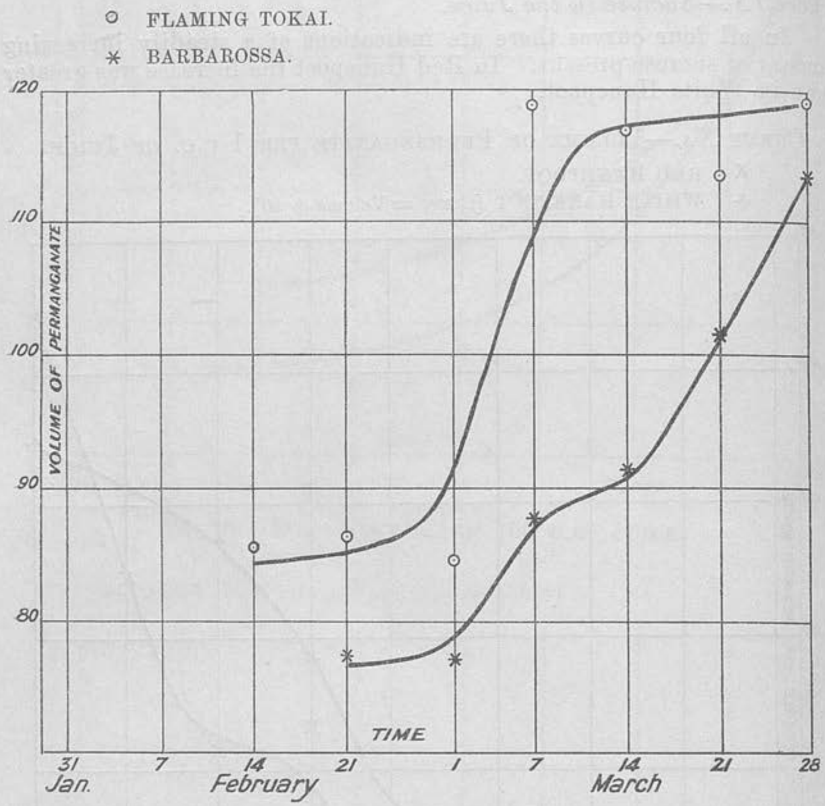
CURVE XA.—VOLUME OF PERMANGANATE PER 1 C.C. OF JUICE.

× RED HANEPOOT.

+ WHITE HANEPOOT [Curve = Volume + 10].



CURVE XB.—VOLUME OF PERMANGANATE PER 1 C.C. OF JUICE.

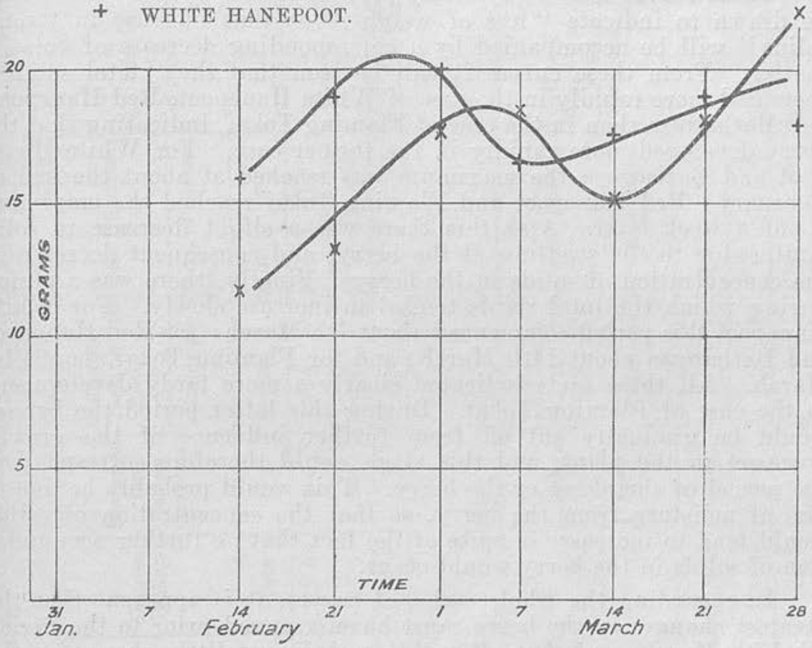


Curve X.—Reducing Substances in the Juice.

All four curves indicate an increase in this factor during the whole season, but they show a peculiarity not shared by any other of the sets of curves, namely, Red Hanepoot and Barbarossa gave similar curves, while the curve for White Hanepoot resembles that for Flaming Tokai. In all four curves, however, there is evidence of a sudden increase in the rate of change at about 1st March owing to the production in the berry of substances which possess reducing properties. In the case of White Hanepoot and Flaming Tokai there were slight indications that an equilibrium was finally attained.

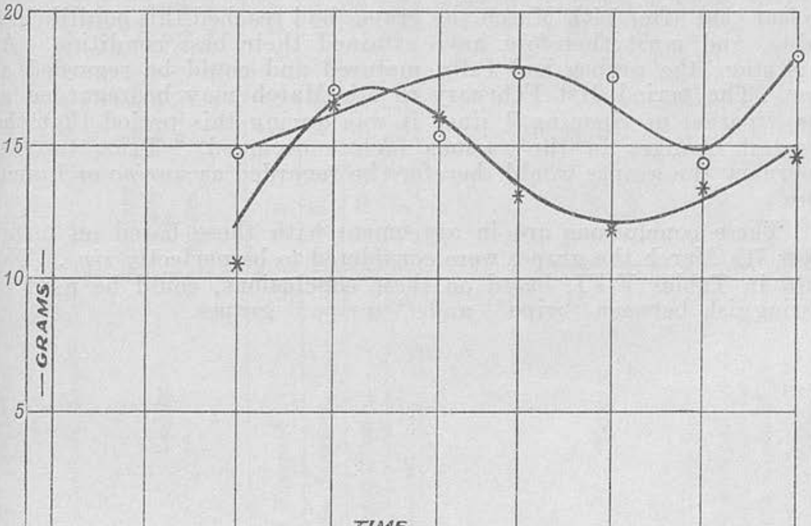
CURVE XIA.—"TOTAL SOLIDS" IN BERRIES.

× RED HANEPOOT.
+ WHITE HANEPOOT.



CURVE XIB.—"TOTAL SOLIDS" IN BERRIES.

⊙ FLAMING TOKAI.
✳ BARBAROSSA.



Curve XI.—"Total Solids" in the Berries.

These curves must be inversely proportional to curves which could be drawn to indicate "loss of weight," so that increase in "total solids" will be accompanied by a corresponding decrease of volatile matter. From these curves it will be seen that the "total solids" increased more rapidly in the case of White Hanepoot, Red Hanepoot, and Barbarossa than in the case of Flaming Tokai, indicating that the berry developed more rapidly in the former case. For White Hanepoot and Barbarossa the maximum was reached at about the end of February; Red Hanepoot and Flaming Tokai reached the maximum about a week later. Afer this there was a slight decrease in solid matter due to the swelling of the berry, and consequent decrease in the concentration of solids in the berry. Finally, there was a period during which the total solids tended to increase slowly. For White Hanepoot this period commenced about 7th March; for Red Hanepoot and Barbarossa about 14th March; and for Flaming Tokai about 21st March. All these facts indicated clearly a more tardy development in the case of Flaming Tokai. During this latter period the berries would be gradually cut off from further influence of the growth processes in the plant, and this stage would therefore correspond to the period of shrinking of the berry. This would probably be due to loss of moisture from the berry, so that the concentration of solids would tend to increase, in spite of the fact that no further accumulation of solids in the berry would occur.

In regarding the whole series of curves, it is apparent that the greatest changes in the berry must have occurred prior to the period 7th-14th March, and that after this period very little change in the constitution occurred. It is clear that, when the grapes have fully matured, some equilibrium must be set up between the various factors which affect the condition of the grape, and that this will not be subject to much further change. From the analytical data it would appear that after 14th March the grapes had reached this equilibrium value, and must therefore have attained their best condition. At this stage the grapes had fully matured and could be regarded as *ripe*. The period 21st February to 7th March may be regarded as the "period of ripening," since it was during this period that the greatest changes in the various factors occurred. Prior to 21st February the grapes would therefore be regarded as *unripe* or immature.

These conclusions are in agreement with those based on taste; after 7th March the grapes were considered to be perfectly *ripe*. The data in Tables V-VI, based on these conclusions, could be used to distinguish between "ripe" and "unripe" grapes.

Table V.

MATURE OR RIPE GRAPES.

Variety.	Average Weight in grams.	Average Volume in c.c.	Volume of Juice from 100 Berries.	Density of Juice.	Degrees Balling.	Hydrogen Ion Concentration.	Acidity as Tartaric Acid.	Glucose.	Sucrose.	C.c. of $N/10\,KMnO_4$ per c.c of Juice.	% Total Solids.
							Grams per 100 c.c. of Grape Juice.				
Red Hanepoot............	6·4	6·0	340	1·084	20·2	3·6	·50	20·0	1·0	120	15·0
White Hanepoot...........	5·9	5·85	320	1·080	19·0	3·8	·55	19·4	1·15	118	17·0
Flaming Tokai............	6·35	6·9	360	1·080	19·0	3·4	·60	19·2	·65	116	15·0
Barbarossa................	5·8	5·5	320	1·070	17·0	3·6	·55	16·8	·85	91	13·0

Table VI.

IMMATURE OR UNRIPE GRAPES.

Variety.	Average Weight in grams.	Average Volume in c.c.	Volume of Juice from 100 Berries.	Density of Juice.	Degrees Balling.	Hydrogen Ion Concentration.	Acidity as Tartaric Acid.	Glucose.	Sucrose.	C.c. of $N/10\,KMnO_4$ per c.c. of Juice.	% Total Solids.
							Grams per 100 c.c. of Grape Juice.				
Red Hanepoot............	5·6	5·35	300	1·070	16·4	3·0	1·00	16·2	·50	105	18·0
White Hanepoot...........	5·1	4·9	265	1·070	16·2	3·3	·90	16·2	·65	80	20·0
Flaming Tokai............	5·6	5·8	275	1·060	14·6	3·3	1·20	14·2	·20	83	17·0
Barbarossa................	4·7	4·4	240	1·055	12·8	3·2	·95	13·0	·60	84	16·0

These figures represent the extreme values, and therefore intermediate figures would correspond to, what might be termed, "the period of ripening." The latter set of figures would, naturally, correspond to the maximum values which the various factors may possess *before* the grapes commence to ripen, and are therefore the *initial* values for the period termed by the French "veraison." Prior to this the grapes would be regarded as "green." After this stage the "degree of ripeness" will depend on individual discretion until the point of maturity is reached, after which the grapes are perfectly mature and no mistake can be made.

Owing to the fact that, when the grapes have become mature, some equilibrium between the various constituents of the berry must be reached, an endeavour was made to determine some numerical relationship which would express this fact. Since glucose and acidity are the most important factors in determining the ripeness of a grape, these quantities were employed to discover this possible relationship. With this idea in mind, Tables XII-XV were calculated from the analytical data and the results graphically represented in Curves XII-XV. In this way some remarkable similarities were brought to light.

Table XII.

Degrees Balling × Average Weight/100.

Date.	Red Hanepoot.	White Hanepoot.	Flaming Tokai.	Barbarossa.
31.1.23..............	·42	—	—	—
7.2.23..............	·80	·64	·70	·52
14.2.23..............	·83	·80	·70	·48
21.2.23..............	1·06	·86	·85	·46
1.3.23..............	1·13	·97	·97	·84
7.3.23..............	1·29	1·08	1·25	·99
14.3.23..............	1·32	1·25	1·21	·95
21.3.23..............	1·50	1·35	1·18	·83
28.3.23..............	1·25	1·26	1·23	·87

Table XIII.

Glucose × Average Weight/100.

Date.	Red Hanepoot.	White Hanepoot.	Flaming Tokai.	Barbarossa.
31.1.23..............	·42	—	—	—
7.2.23................	·74	·63	·59	·46
14.2.23..............	·73	·78	·66	·42
21.2.23..............	1·00	·84	·78	·41
1.3.23................	1·13	1·01	·86	·69
7.3.23................	1·25	1·15	1·22	1·00
14.3.23..............	1·29	1·30	1·22	·92
21.3.23..............	1·46	1·37	1·22	·83
28.3.23..............	1·30	1·31	1·26	·87

Table XIV.

Glucose/" Total Solids."

Date.	Red Hanepoot.	White Hanepoot.	Flaming Tokai.	Barbarossa.
31.1.23..............	—	—	—	—
7.2.23................	—	—	—	—
14.2.23..............	1·18	1·13	1·00	1·04
21.2.23..............	1·25	·84	·80	·69
1.3.23................	1·02	·94	·91	·83
7.3.23................	1·06	1·17	1·17	1·30
14.3.23..............	1·33	1·24	1·16	1·36
21.3.23..............	1·27	1·26	1·32	1·22
28.3.23..............	1·10	1·41	1·12	1·29

Table XV.

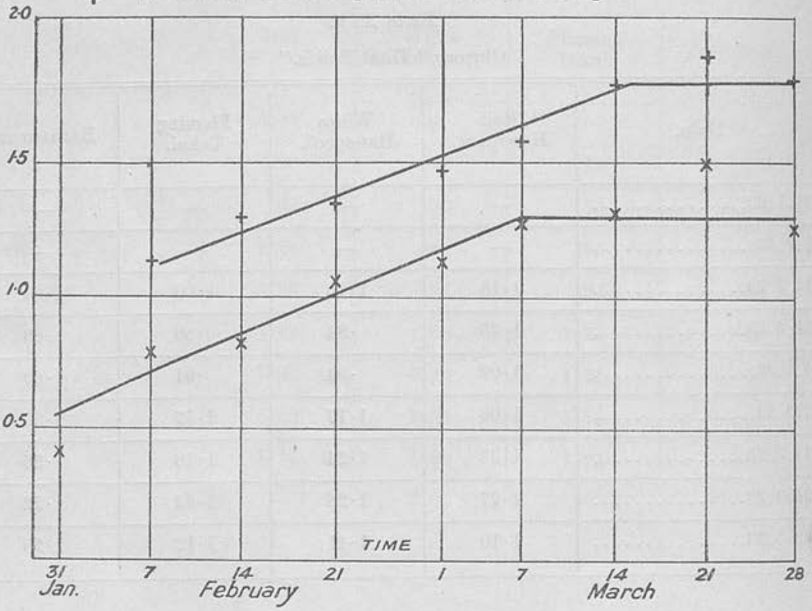
Acidity × 10/Glucose.

Date.	Red Hanepoot.	White Hanepoot.	Flaming Tokai.	Barbarossa.
31.1.23	1·87	—	—	—
7.2.23	·64	·94	1·31	1·00
14.2.23	·76	·72	·88	1·10
21.2.23	·52	·53	·89	·82
1.3.23	·38	·37	·67	·57
7.3.23	·31	·35	·36	·38
14.3.23	·27	·26	·32	·38
21.3.23	·20	·21	·31	·28
28.3.23	·22	·21	·21	·24

CURVE XIIA.—BALLING × AVERAGE WEIGHT / 100.

× RED HANEPOOT.

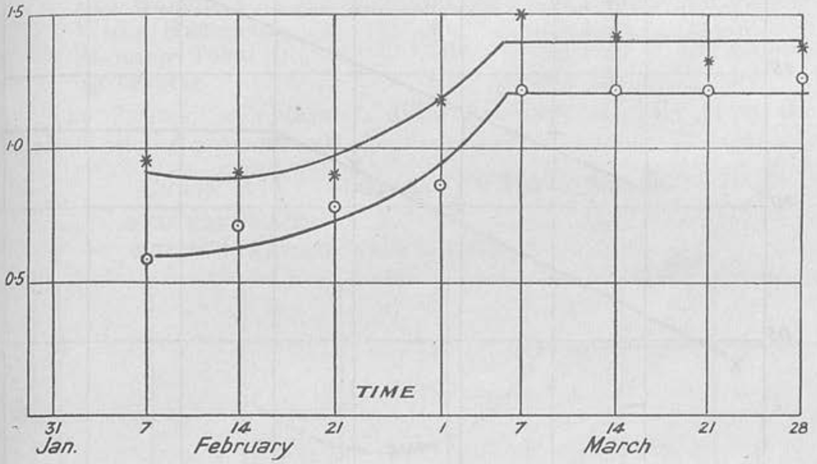
+ WHITE HANEPOOT [Curve = Product + 0·5].



CURVE XIIB.—BALLING × AVERAGE WEIGHT / 100.

⊙ FLAMING TOKAI.

✱ BARBAROSSA [Curve = Product + 0·5].



Curve XII.—Degrees Balling × Average Weight ÷ 100.

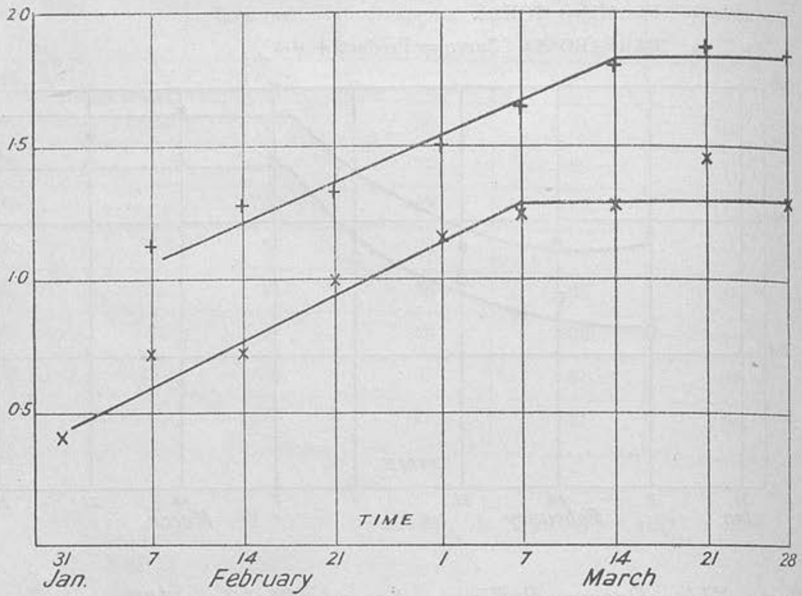
In all cases the curves tend to reach a limiting value at a period agreeing with the period of maturity deduced from the previous sets of curves. The relationship is a measure of the total yield of sugar possible from a given number of grapes, and it would be expected that a maximum would be reached when the grapes were ripe. Once this maximum is reached, it is clear, from the curves, that there was practically no further production of sugar. The great resemblance between Red Hanepoot and White Hanepoot is brought out plainly by the curves. It is evident that the yield of sugar from the Red and White Hanepoots was practically identical and greater than that from the other two varieties. In other words, the two former varieties tended to be sweeter than the two latter. Combining these curves with the information obtained from the preceding sets of curves, the following data may be deduced for fixing the different stages of development of the grapes:—

	Green less than	Ripening.	Ripe equal to or greater than
Red Hanepoot	.90	.90–1.30	1.30
White Hanepoot ...	.90	.90–1.30	1.30
Flaming Tokai... ...	.80	80–1.20	1.20
Barbarossa	.60	.60– .90	.90

CURVE XIIIA.—GLUCOSE × AVERAGE WEIGHT / 100.

× RED HANEPOOT.

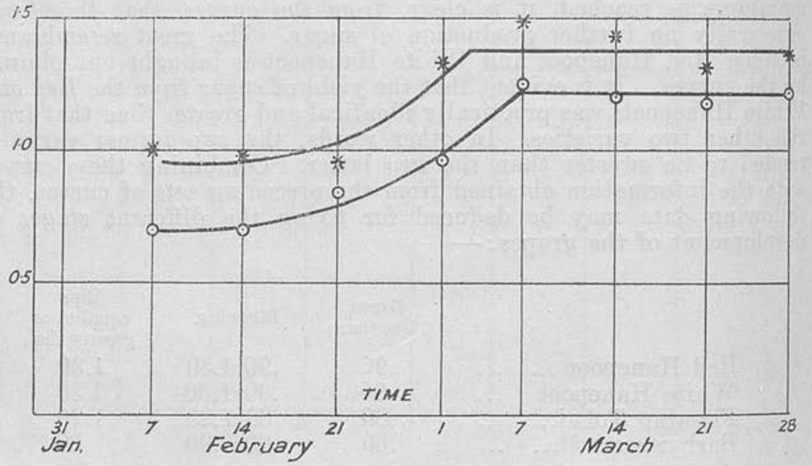
+ WHITE HANEPOOT [Curve = Product + 0·5].



CURVE XIIIB.—GLUCOSE × AVERAGE WEIGHT / 100.

○ FLAMING TOKAI.

✳ BARBAROSSA [Curve = Product + 0·5].



Curve XIII.—Glucose × Average Weight ÷ 100.

These curves show the same characteristics as the previous curves, and the same remarks are applicable to them, so that the following data may be deduced:—

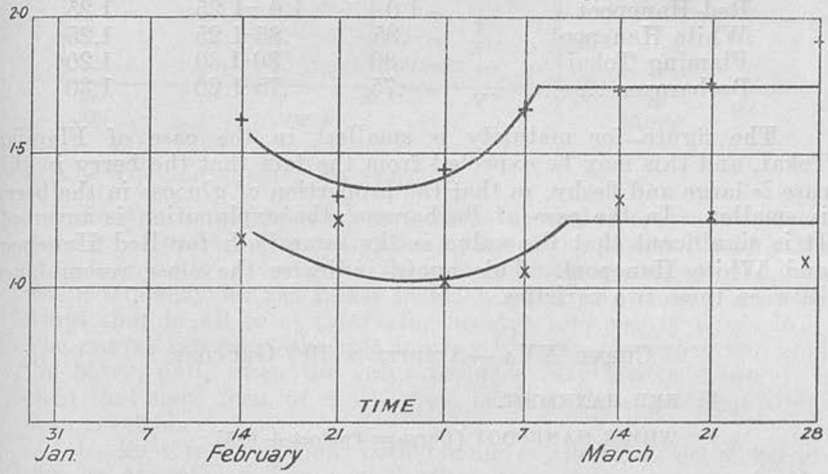
	Green less than	Ripening.	Ripe equal to or greater than
Red Hanepoot	.90	.90-1.30	1.30
White Hanepoot ...	.80	.80-1.30	1.30
Flaming Tokai... ...	.70	.70-1.20	1.20
Barbarossa	.45	.45- .90	.90

The figures, so obtained, differ but very slightly from those obtained in the previous set.

Curve XIVa.—Glucose / "Total Solids."

× RED HANEPOOT.

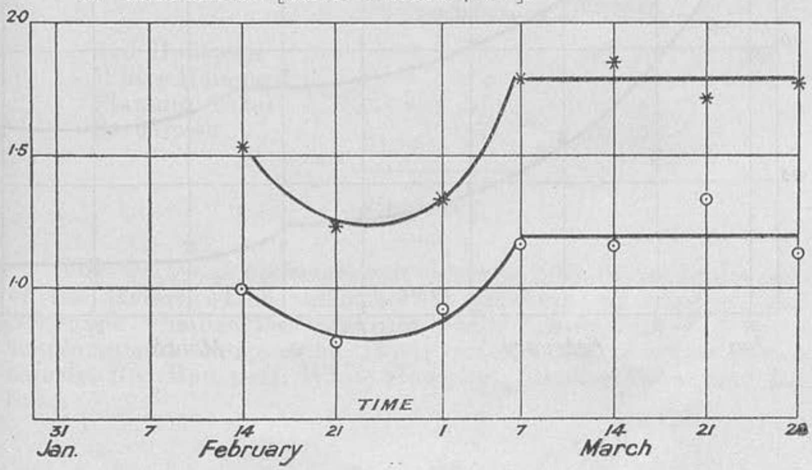
+ WHITE HANEPOOT [Curve = Product + 0·5].



Curve XIVb.—Glucose / "Total Solids."

⊙ FLAMING TOKAI.

✱ BARBAROSSA [Curve = Product + 0·5].



Curve XIV.—Glucose / "Total Solids."

These curves represent the proportion of glucose present in the berry to the total constituents of the berry. When maturity is reached it is to be expected that equilibrium has been reached, so that little change in this ratio would be expected. The curves fully bear out these conclusions, and the final portions of the curves represent the limiting value of this equilibrium. This value was reached about 7th March, and is fully in accordance with the period for the initial stages of maturity as deduced from the other curves. In the initial stages the ratio decreases, indicating that the growth of other constituents is more rapid than the accumulation of sugar.

Using the data regarding the period of ripening, we may deduce the following data:—

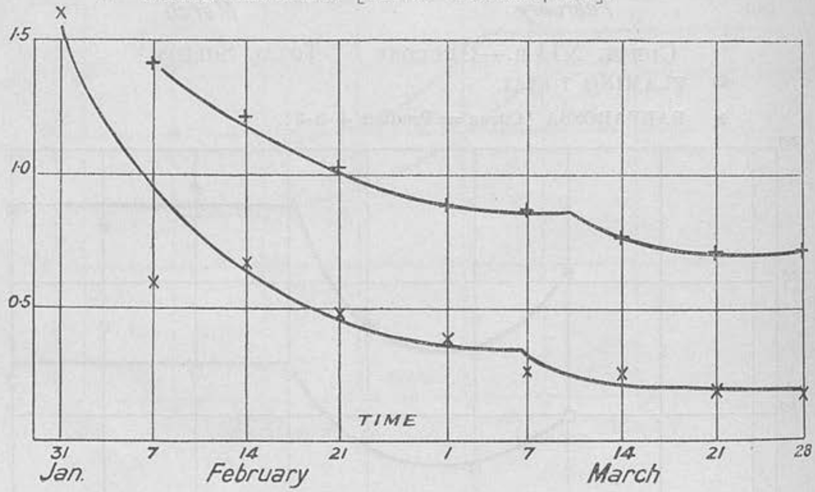
	Green.	Ripening.	Ripe equal to or greater than
Red Hanepoot	– 1.0	1.0 –1.25	1.25
White Hanepoot ...	– .85	.85–1.25	1.25
Flaming Tokai	– .80	.80–1.30	1.20
Barbarossa	– .75	.75–1.20	1.30

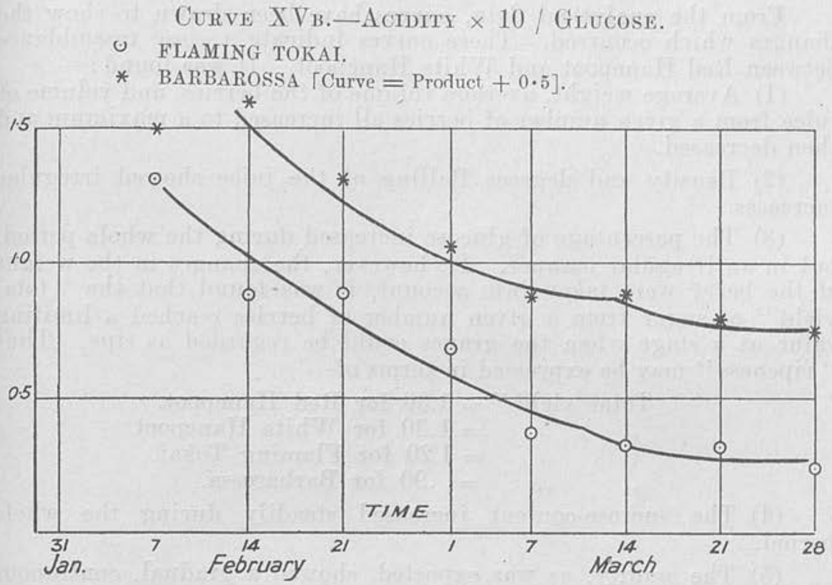
The figure for maturity is smallest in the case of Flaming Tokai, and this may be expected from the fact that the berry in this case is large and fleshy, so that the proportion of glucose in the berry is smaller. In the case of Barbarossa, the explanation is reversed. It is significant that the value is the same both for Red Hanepoot and White Hanepoot. This again indicates the close resemblance between these two varieties.

Curve XVa.—Acidity × 10 / Glucose.

× RED HANEPOOT.

+ WHITE HANEPOOT [Curve = Product + 0·5].





Curve XV.—Acidity × 10 / Glucose.

As was to be expected, this value showed a continuous decrease during the period of investigation. About the period 7th-14th March there was a slight change in the rate of decrease, and after this there was a tendency for the factor to reach a limiting value. It is significant that in all cases this value became very nearly equal to 0.20. The curves represent the relationship between the sugar and acid in the berry, and, when the value becomes very nearly constant, it is clear that some form of equilibrium between these two quantities has been reached.

Under these conditions little change in the condition of the grape can be expected. The period when this stage is reached, agrees very well with that obtained by examining the other curves. Therefore the following data may be deduced:—

	Green greater than	Ripening.	Ripe equal to or less than
Red Hanepoot	.50	.50–.25	.25
White Hanepoot	.50	.50–.25	.25
Flaming Tokai	.75	.75–.30	.30
Barbarossa	.70	.70–.25	.25

SUMMARY.

This work was undertaken to obtain an idea of the limits of some of the factors which influence the condition of ripeness, and to determine whether this condition could not be expressed by some simple numerical expression. Four varieties of grapes were employed, namely, Red Hanepoot, White Hanepoot, Flaming Tokai, and Barbarossa.

From the analytical data, curves have been drawn to show the changes which occurred. These curves indicate a close resemblance between Red Hanepoot and White Hanepoot. It was found :—

(1) Average weight, average volume of the berries, and volume of juice from a given number of berries all increased to a maximum and then decreased.

(2) Density and degrees Balling of the juice showed irregular increases.

(3) The percentage of glucose increased during the whole period, but in an irregular manner. If, however, the changes in the weight of the berry were taken into account, it was found that the "total yield" of sugar from a given number of berries reached a limiting value at a stage when the grapes could be regarded as ripe. Thus "ripeness" may be expressed in terms of—

"Total yield" = 1.30 for Red Hanepoot.
,, ,, = 1.30 for White Hanepoot.
,, ,, = 1.20 for Flaming Tokai.
,, ,, = .90 for Barbarossa.

(4) The sucrose-content increased steadily during the whole period.

(5) The acidity, as was expected, showed a gradual, continuous decrease during the whole period, but this decrease was not in direct inverse proportion to the increase in glucose. There seemed to be a tendency for the proportion of acid to glucose to arrive at a limiting value of 0.20.

The hydrogen-ion concentration of the juice increased steadily.

(6) The changes in "total solids" could be explained by the swelling and shrinking of the berry.

From all the data that had been collected it was concluded that the various factors had very nearly reached an equilibrium value by the end of the first week in March, and the grapes would be regarded as "ripe." From 21st February to 7th March was regarded as the "period of ripening." Numerical expressions were derived to determine these periods.

In conclusion, the author would like to express his acknowledgment and thanks to Messrs. W. J. Copenhagen and F. J. Dillman, Officers of the Chemistry Division, Capetown, for assistance in carrying out a large number of the analyses necessary for this paper. The author would also like to acknowledge gratefully the assistance of Mr. Van Reenen, of the Government Wine Farm, in placing the facilities of the farm at our disposal.

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SOME CHANGES OCCURRING DURING THE RIPENING OF GRAPES

(THIRD PAPER)

BY

P. R. v. d. R. COPEMAN, B.A., B.Sc. D.Sc. 192

Division of Chemistry, Capetown

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SOME CHANGES OCCURRING DURING THE RIPENING OF GRAPES.

(THIRD PAPER).

By P. R. v. d. R. Copeman, B.A., B.Sc., Division of Chemistry, Capetown.

On account of the early completion of the vintage in 1925 the work * carried out in connexion with the changes occurring during the ripening of grapes was extended over a comparatively limited period. It was, therefore, felt that further work was necessary in order to obtain some idea of the limits between which the factors governing the ripeness of the fruit may vary. It was particularly necessary to examine the variations which might occur during the period of maturity and to investigate more closely the initial changes which take place prior to the onset of ripening. For these reasons the present work embodying the results of the investigation of the 1926 vintage was undertaken. The work was commenced as early in the year as possible and extended from 13th January to 24th March. In this way a comparison of the present results could be made with the results obtained in 1923 † and 1925.

In comparison with the two previous years (1923 and 1925) the climatic conditions during the present season formed a decided contrast. In 1923 no rain fell during the period of investigation, and the days were clear and warm. In 1925, the total rainfall during the period of investigation was only 0·21 inch, and this occurred on two separate days about a week apart and near the beginning of the ripening period. In both years, therefore, the conditions for plant development were favourable. In 1926 the total rainfall of 2·10 inches occurred on seven days during the investigation, and there were a large number of cloudy days. The mean temperature was also higher during 1925 than during 1926. The conditions, therefore, during the present season did not favour the development of the plants. On this account the period of ripening was prolonged and the attainment of maturity somewhat delayed.

In this connexion a paper ‡ dealing with "Some Effects of Seasonal Conditions upon the Chemical Composition of American Grape Juices" appeared during 1925 in which considerable variations were recorded for different seasons. It is stated "that there is a consistent and fairly high

* Copeman and Frater, Dept. of Agric. Sc. Bull. No. 50, 1926.
† Copeman, Dept. of Agric. Bull., Div. of Chem. Series No. 31, 1924.
‡ Caldwell, J., Agr. Res. Vol. 30, No. 12, 1925, 1133.

degree of correlation between sugar, acid, and total astringent content." Therefore, since the ripeness of the fruit depends mainly upon these factors, it is important that when the results for different seasons are compared, the fruit should be at the same stage of maturity. In this paper, however, there seems to be little connexion between the season and the date of picking. In unfavourable years the period of maturity tends to be delayed, and no account has been taken of this factor. The conclusions, therefore, are open to objection on this ground.

As appeared clearly in the work in 1925,* a number of determinations were made which could not be correlated with the stages of ripeness in the berries. Such factors as average volume, average weight, seeds in berry, etc., are subject to variations which do not affect the quality of the fruit. They are of limited application in practice, and, therefore, the present work has been limited to an examination of factors such as acidity and sugar-content. These factors have the greatest influence upon the quality of the fruit, and their importance justifies the most careful examination of the changes which they undergo.

For the present investigation the same six varieties of table grapes were used as in 1925, namely, White Hanepoot, Red Hanepoot, Gros Maroc, Barbarossa, Waltham Cross, and Flaming Tokai. The samples were obtained from the Government wine farm, Groot Constantia, and the analytical work carried out in the Government Chemical Laboratories, Capetown. Through the kindness of the manager the samples were forwarded regularly once a week during the period of investigation. This period allowed an examination to be made of the changes which occur (*a*) before the commencement of the ripening period, (*b*) after the initial attainment of maturity.

From the bunches as received an average sample was obtained of sufficient weight to yield about 250 c.c. of juice. The subsequent treatment and, except as outlined below, the various determinations were the same as described in the previous work.* The hydrogen-ion concentration ($_{p}H$) of the juice was determined colorimetrically. The "soluble solids" in the juice was estimated by evaporating 25·0 c.c. on a water-bath and finally heating to dryness in an electric oven at 100° C. The results, expressed as "soluble solids per 100 grammes of juice," served to check the readings of the Balling Hydrometer.

The "astringency" was estimated by the oxidation method using potassium permanganate and indigo-carmine. The results were expressed in terms of tannin per 100 c.c. juice, and included such materials as true tannin and colouring matter. The conductivity of the juice was determined by the Wheatstone Bridge method.

The "total solids in the berry" was determined by halving a sufficient number of berries and using only one half of each berry. The loss in weight was estimated by placing the dish in an electric oven at 100° C. for twenty-four hours. Independent experiment had shown that after this period there was a small but constant rate of loss of about 0·05 per cent. per hour. This was ascribed to the commencement of decomposition of the carbo-hydrates, especially sugars, present in the juice. On this account twenty-four hours was chosen as the standard time of heating under these conditions. It was seen that this method was applicable to all the varieties. The residue from this determination was used to determine the ash in the berry.

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* *Loc. cit.*

The results of the examination of the juice are given in Tables I–VI.

TABLE I.—WHITE HANEPOOT.

Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice × 10³.
13/1/26	49·5	47·9	1·0189	4·8	3·25	2·3	1·55	·077	4·35	—
20/1/26	51·0	45·3	1·0278	7·0	3·25	2·3	3·68	·068	6·53	4·8
27/1/26	50·0	45·9	1·0424	10·5	2·25	2·6	7·93	·060	9·50	4·7
3/2/26	48·3	46·5	1·0491	12·2	1·90	2·8	9·98	·088	11·97	4·5
10/2/26	47·3	47·4	1·0505	12·7	1·61	2·9	10·75	·066	12·61	3·5
17/2/26	48·0	46·3	1·0658	16·4	1·01	3·2	14·74	·039	16·13	3·1
24/2/26	47·0	47·1	1·0728	17·7	·89	3·5	16·66	·049	17·89	3·1
3/3/26	50·1	44·0	1·0768	19·0	·77	3·6	18·03	·046	19·15	2·7
10/3/26	45·0	47·3	1·0918	22·0	·70	3·7	21·52	·047	22·08	3·1
17/3/26	49·3	44·3	1·0850	20·8	·64	3·8	19·83	·053	20·50	3·1
24/3/26	51·5	41·5	1·0933	22·3	·60	3·9	21·66	·057	22·00	2·6

TABLE II.—RED HANEPOOT.

Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice × 10³.
13/1/26	48·0	49·6	1·0199	5·1	3·30	2·3	1·55	·074	4·83	—
20/1/26	57·8	38·3	1·0252	6·4	3·34	2·3	2·78	·079	5·92	4·8
27/1/26	46·8	48·9	1·0410	10·0	2·46	2·4	7·63	·056	8·94	4·5
3/2/26	46·6	48·7	1·0508	12·6	1·81	2·9	10·49	·063	12·70	4·4
10/2/26	47·1	48·6	1·0542	13·9	1·70	2·9	11·74	·070	13·88	3·6
17/2/26	48·1	46·3	1·0656	16·2	1·10	3·2	14·67	·039	16·23	3·3
24/2/26	48·6	44·9	1·0742	18·0	1·01	3·5	16·87	·049	18·16	2·6
3/3/26	50·6	43·3	1·0807	20·1	·73	3·7	19·08	·048	20·30	2·9
10/3/26	52·0	41·3	1·0826	20·3	·72	3·7	19·55	·043	20·28	2·7
17/3/26	52·7	41·0	1·0780	19·1	·64	3·7	18·47	·046	19·52	3·1
24/3/26	55·9	36·4	1·0882	21·6	·54	3·8	20·84	·051	21·84	2·9

TABLE III.—GROS MAROC.

Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice × 10³.
13/1/26	50·4	47·4	1·0207	5·3	3·67	2·2	1·33	·065	4·72	—
20/1/26	48·9	47·6	1·0204	5·2	3·65	2·2	1·36	·074	5·09	5·5
27/1/26	48·5	49·1	1·0223	5·7	3·64	2·2	1·80	·055	5·34	5·0
3/2/26	49·7	46·2	1·0277	7·0	3·56	2·3	3·18	·055	6·67	5·3
10/2/26	58·4	36·9	1·0376	9·4	2·81	2·5	6·58	·055	9·36	4·5
17/2/26	63·0	31·5	1·0459	11·9	2·29	2·7	8·70	·044	11·65	4·0
24/2/26	59·4	35·0	1·0582	14·4	1·69	3·1	12·65	·058	14·23	2·8
3/3/26	58·9	35·3	1·0617	15·7	1·57	3·2	13·49	·062	15·87	3·1
10/3/26	67·1	25·8	1·0667	16·8	1·14	3·4	15·33	·056	17·03	2·7
17/3/26	64·8	28·3	1·0681	17·3	1·12	3·4	15·80	·053	17·37	3·0
24/3/26	61·8	31·8	1·0684	17·3	1·07	3·4	15·40	·059	17·44	2·9

Table IV.—Barbarossa.

Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice $\times 10^3$.
13/1/26	47·9	50·2	1·0183	4·7	2·97	2·3	1·41	·112	4·36	—
20/1/26	58·3	38·9	1·0201	5·3	3·06	2·3	1·82	·109	4·85	5·5
27/1/26	52·9	44·9	1·0194	5·0	3·12	2·2	1·70	·083	5·13	5·1
3/2/26	47·6	48·1	1·0292	7·4	2·75	2·5	4·36	·094	7·46	4·9
10/2/26	53·8	41·5	1·0453	11·6	1·92	2·6	9·24	·091	11·25	3·7
17/2/26	60·2	34·9	1·0522	12·8	1·54	3·0	11·12	·056	12·74	2·6
24/2/26	58·9	35·0	1·0612	15·3	1·20	3·3	13·80	·058	15·20	2·7
3/3/26	57·1	36·4	1·0650	16·3	1·09	3·3	14·91	·053	16·25	2·7
10/3/26	57·6	35·2	1·0703	17·6	·96	3·5	16·48	·046	17·77	3·1
17/3/26	58·8	35·7	1·0751	18·5	·90	3·5	17·39	·057	18·71	3·1

Table V.—Waltham Cross.

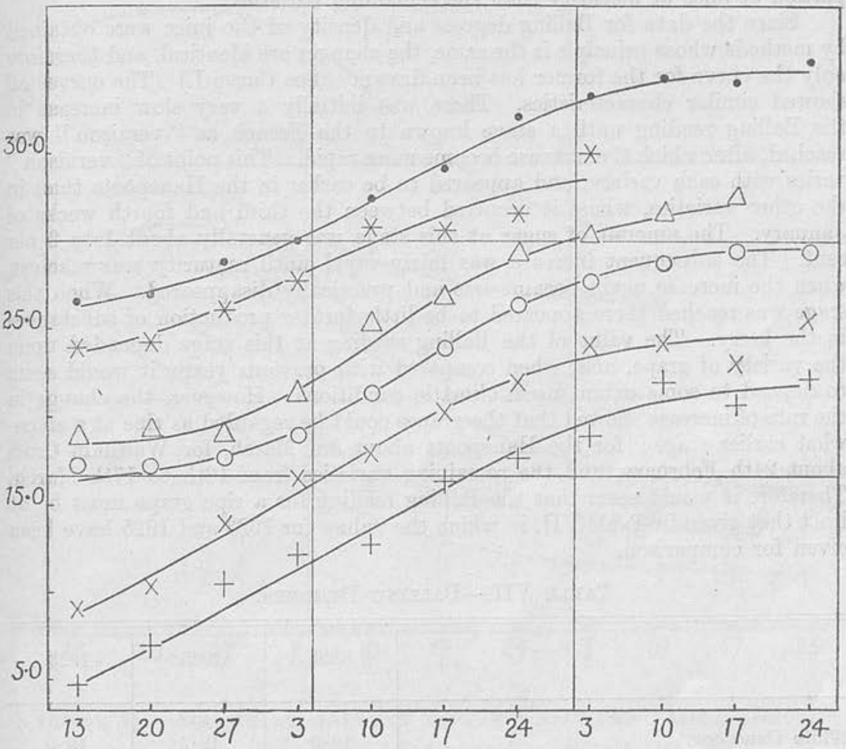
Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice $\times 10^3$.
13/1/26	41·9	55·2	1·0314	7·9	2·82	2·4	4·87	·134	7·44	—
20/1/26	58·1	37·7	1·0324	8·2	2·53	2·4	5·20	·112	7·86	4·3
27/1/26	48·5	47·2	1·0405	10·1	2·02	2·6	7·96	·086	9·05	4·2
3/2/26	55·7	39·1	1·0473	11·8	1·49	3·0	9·86	·092	11·83	4·4
10/2/26	56·2	38·0	1·0587	14·8	1·25	3·1	13·16	·097	14·82	3·8
17/2/26	61·6	32·5	1·0575	14·6	1·21	3·2	12·67	·070	14·44	3·6
24/2/26	57·8	35·8	1·0636	15·6	·98	3·5	14·24	·056	15·65	3·4
3/3/26	55·6	37·2	1·0771	19·0	·82	3·5	17·93	·074	19·30	3·2
10/3/26	—	—	—	—	·72	3·8	19·60	—	20·45	—

Table VI.—Flaming Tokai.

Date.	Volume of juice per 100 grammes berry.	Weight of residue per 100 grammes berry.	Density of juice at 20° C.	Balling.	Acidity as grammes tartaric acid per 100 c.c.	pH.	Glucose in grammes per 100 c.c.	Astringency as grammes tannin per 100 c.c.	Soluble solids in grammes per 100 grammes.	Conductivity of juice $\times 10^3$.
13/1/26	47·4	49·7	1·0179	4·6	3·40	2·2	0·93	·133	4·22	—
20/1/26	53·1	44·6	1·0191	4·9	3·58	2·2	1·19	·130	4·71	4·8
27/1/26	42·8	54·7	1·0267	6·8	3·54	2·2	3·21	·069	6·75	5·1
3/2/26	47·9	48·0	1·0318	8·0	3·42	2·2	4·95	·084	7·68	5·0
10/2/26	55·2	39·6	1·0400	10·4	2·67	2·4	7·16	·071	10·21	4·2
17/2/26	55·8	40·0	1·0460	12·1	2·07	2·6	8·90	·071	11·93	3·9
24/2/26	55·4	38·8	1·0598	15·1	1·46	3·2	12·49	·050	15·00	3·3
3/3/26	56·8	37·3	1·0646	16·3	1·15	3·4	14·61	·051	16·34	3·4
10/3/26	57·5	36·1	1·0693	17·3	·98	3·6	16·01	·050	17·68	3·1
17/3/26	57·8	35·9	1·0673	17·1	·85	3·6	15·45	·048	17·13	3·1
24/3/26	64·0	28·5	1·0739	18·3	·80	3·7	16·86	·058	18·22	3·1

Since the analytical data give the same general types of curves as previously obtained, the attempt to follow the changes by means of curves has not been adopted in every case. The question regarding the value to be placed upon any regular curve to represent the changes which occur has been already fully discussed in a previous paper.* In the present case only a limited number of curves has been drawn, and they will be discussed in their order.

In comparing the results for "Yield of Juice" with those for 1925, it was seen that they were considerably lower in the present instance. The discrepancies were so large that the only conclusion that could safely be drawn was that the method adopted for estimating this factor was subject to large errors. The fact that the values for any given variety of grape were subject to great irregularities among themselves also pointed to this source of error.



CURVE I.—BALLING DEGREES OF THE JUICE.

+ White Hanepoot.
× Red Hanepoot............................ Curve = Balling + 4·0
○ Gros Maroc............................ Curve = Balling + 12·0
△ Barbarossa............................ Curve = Balling + 14·0
★ Waltham Cross............................ Curve = Balling + 16·0
● Flaming Tokai............................ Curve = Balling + 22·0

In practice it was found that when the residue from the fruit press was subjected to further pressure by hand an additional quantity of juice could be obtained. Furthermore, the quantity so obtained varied for each variety in a very

* Copeman and Frater, *loc. cit.*

irregular manner from 10 per cent. to 40 per cent. of the total juice obtained. Furthermore the quantity so obtained varied for each variety in a very irregular manner from 10 per cent. to 40 per cent. of the total juice obtained. No relationship of any sort could be found to account for these variations. It would, therefore, seem that, unless the press were so constituted that uniform and comparable pressures were obtained, no reliance can be placed upon the figures obtained in this way for the yield of juice. This is so much the case that under the present conditions the method is of little practical value as a means of following the changes in the degree of ripeness. These remarks apply equally to the value to be placed upon the weight of residue formed. Under these circumstances any ratios obtained, which include as a factor "Yield of Juice," will be subject to the same source of error. The only safe conclusion that could be drawn was that the more fleshy berries tended to yield a lower proportion of juice at maturity than the remaining varieties.

Since the data for Balling degrees and density of the juice were obtained by methods whose principle is the same, the changes are identical, and therefore only the curve for the former has been drawn. (See Curve I.) The curves all showed similar characteristics. There was initially a very slow increase in the Balling reading until a stage known to the French as "veraison" was reached, after which the increase became more rapid. This point of "veraison" varies with each variety, and appeared to be earlier in the Hanepoots than in the other varieties, where it occurred between the third and fourth weeks of January. The amount of sugar at this stage was generally about 1 to 2 per cent. The subsequent increase was fairly rapid until maturity was reached, when the increase again became less and practically disappeared. When this stage was reached there appeared to be little further production of substances in the berry. The value of the Balling reading at this stage depended upon the variety of grape, and, when compared with previous years, it would seem to depend to some extent upon climatic conditions. However, the change in the rate of increase showed that the grapes could be regarded as ripe at a somewhat earlier stage; for the Hanepoots about 3rd March, for Waltham Cross about 24th February, and the remaining varieties from 10th to 17th March. Therefore it would seem that the Balling reading for a ripe grape must be at least that given in Table VII, in which the values for 1923 and 1925 have been given for comparison.

TABLE VII.—BALLING DEGREES.

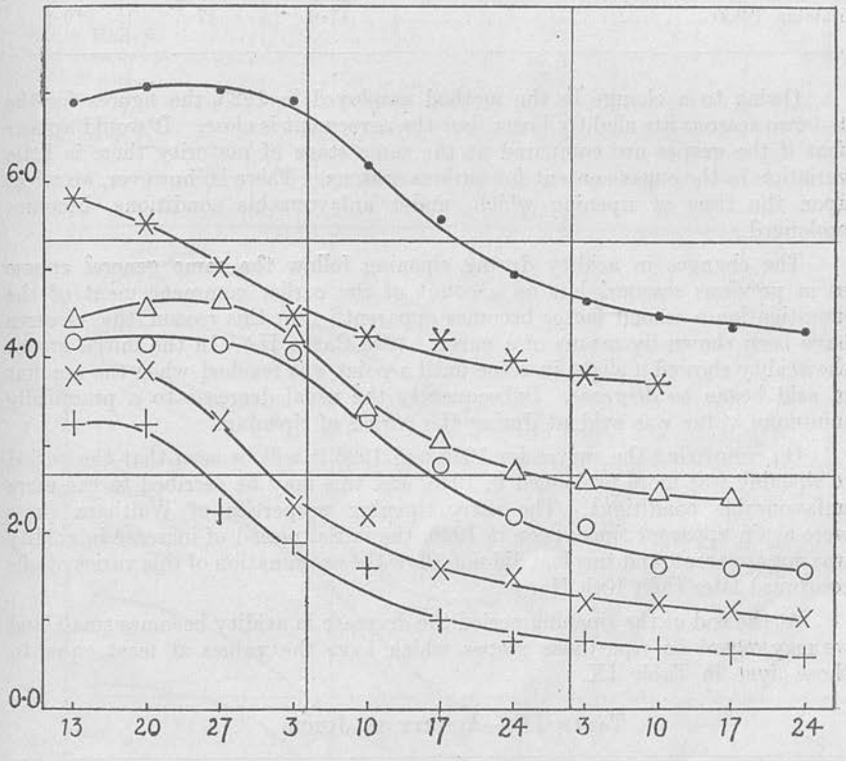
	1926.	1925.	1923.
White Hanepoot	19·0	19·5	19·0
Red Hanepoot	19·0	19·8	20·2
Gros Maroc	17·3	18·6	—
Barbarossa	17·5	17·0	17·0
Waltham Cross	16·0	16·8	—
Flaming Tokai	17·0	19·3	19·0

These figures show a very good agreement among themselves and indicate that for a ripe grape the Balling reading of the juice must lie between fairly close limits according to the variety.

The changes which occurred also resembled very closely the changes in 1925, except that the initial slow increase was not clearly evident in the latter year, and that the period of maturity in 1926 was more prolonged.

On examining the changes which occurred in the sugar-content of the juice, it was seen that they followed the course of the Balling degrees so closely that no attempt has been made to include a curve to show these changes. There was an initial slow increase to the stage of the "verasion," later a more rapid increase, corresponding to the period of ripening, and finally the increase became very slow or practically disappeared—the period of maturity.

It is thus evident that after ripeness has been attained, the changes in sugar-content are slight and this stage is particularly evident in the present



CURVE II.—ACIDITY AS GRAMMES TARTARIC ACID PER 100 C.C. JUICE.

+ White Hanepoot.
× Red Hanepoot.......................... Curve = Acid + 0·5
○ Gros Maroc.......................... Curve = Acid + 0·5
△ Barbarossa.......................... Curve = Acid + 1·5
★ Waltham Cross.......................... Curve = Acid + 3·0
● Flaming Tokai.......................... Curve = Acid + 3·5

results. This stage was reached at different times according to the variety of the grape: For the Hanepoots about 10th March, for Gros Maroc and Barbarossa somewhat later, and for Waltham Cross about 17th January. However, it may be concluded that for the grapes to be considered ripe, the sugar-content must be at least that given in Table VIII.

TABLE VIII.—GLUCOSE IN JUICE.

	1926.	1925.	1923.
White Hanepoot	18·0	18·4	18·8
Red Hanepoot	18·5	19·0	19·5
Gros Maroc	15·4	17·0	—
Barbarossa	16·0	16·5	16·3
Waltham Cross	15·5	16·0	—
Flaming Tokai	17·0	17·5	19·2

Owing to a change in the method employed in 1923, the figures for the last two seasons are slightly lower, but the agreement is close. It would appear that if the grapes are compared at the same stage of maturity there is little variation in the sugar-content for various seasons. There is, however, an effect upon the time of ripening which, under unfavourable conditions, becomes prolonged.

The changes in acidity during ripening follow the same general course as in previous seasons, but on account of the earlier commencement of the investigation a second factor becomes apparent. For this reason the changes have been shown by means of a curve. (See Curve II.) In the initial stages the acidity showed a slight increase until a point was reached when the amount of acid began to decrease. Subsequently the usual decrease to a practically minimum value was evident during the period of ripening.

On comparing the curves for 1925 and 1926 it will be seen that the period of ripening was more prolonged in 1926, and this may be ascribed to the more unfavourable conditions. The early ripening properties of Waltham Cross were again apparent since, even in 1926, the initial period of increase in acidity was not apparent, and this fact did not allow the examination of this variety to be continued later than 10th March.

At the end of the ripening period the decrease in acidity becomes small, and we may regard as ripe those grapes which have the values at least equal to those given in Table IX.

TABLE IX.—ACIDITY IN JUICE.

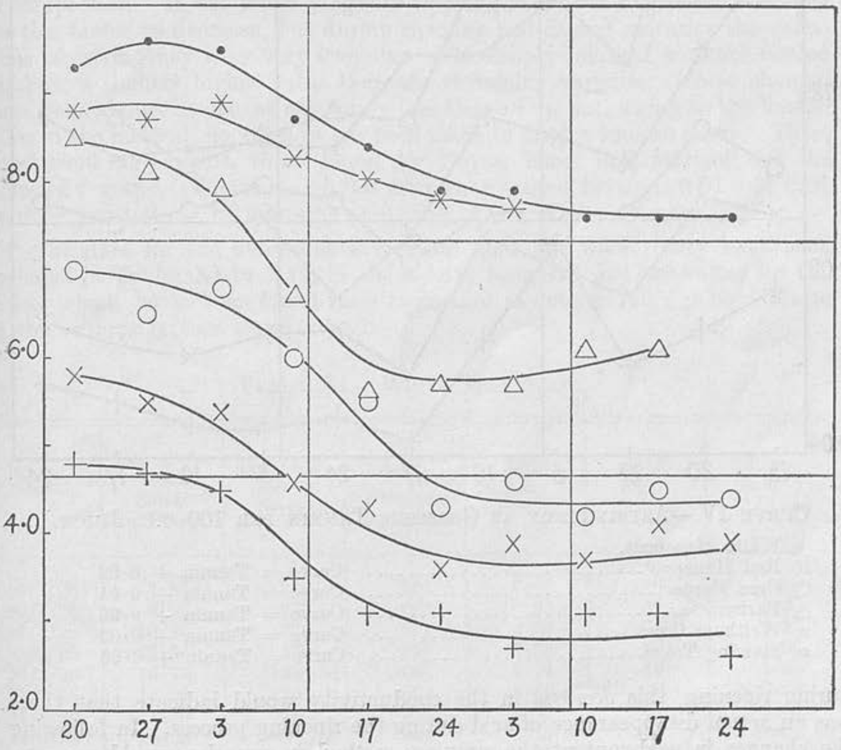
	1926.	1925.	1923.
White Hanepoot	·70	·70	·60
Red Hanepoot	·73	·70	·55
Gros Maroc	1·05	·90	—
Barbarossa	·95	·67	·60
Waltham Cross	·80	·90	—
Flaming Tokai	·90	·75	·70

During these three years conditions both favourable and unfavourable have been experienced, and the differences are not unduly large. It would appear that maturity is characterized by a definite concentration both of acid and of sugar. The nature of this relationship will be discussed in a later paper.

In the case of the hydrogen-ion concentration of the juice the changes followed the changes in acidity as determined by titration. The values for ripe grapes are given in Table X with the values for previous years for comparison.

TABLE X.—HYDROGEN-ION CONCENTRATION.

	1926.	1925.	1923.
White Hanepoot	3·7	3·6	3·6
Red Hanepoot	3·7	3·4	3·8
Gros Maroc	3·4	3·2	—
Barbarossa	3·5	3·6	3·6
Waltham Cross	3·5	3·6	—
Flaming Tokai	3·6	3·6	3·4

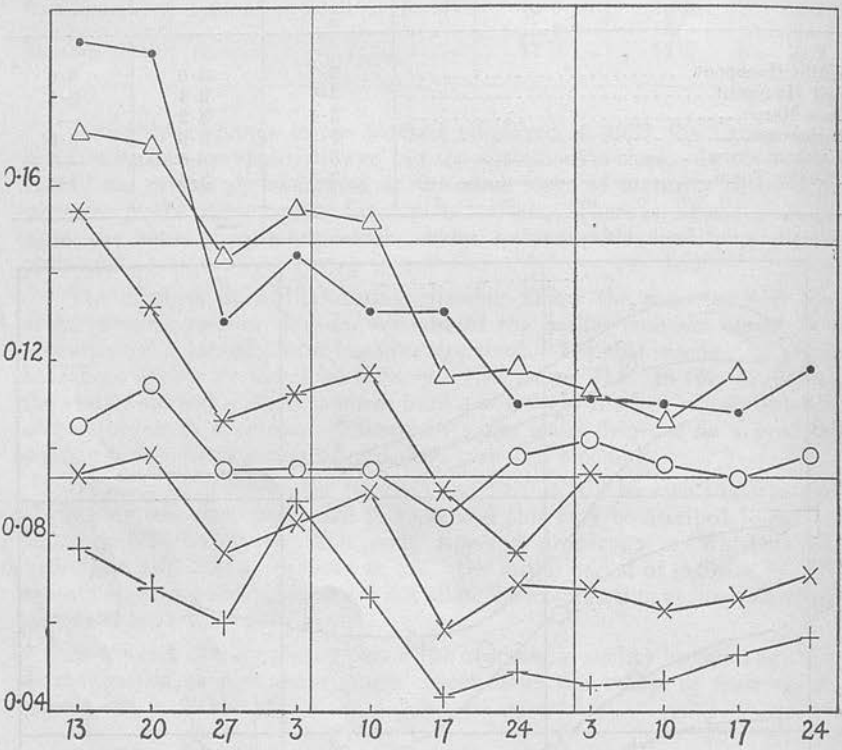


CURVE III.—CONDUCTIVITY OF JUICE × 10³.

+ White Hanepoot.
× Red Hanepoot........................ Curve = Conductivity + 1·0
○ Gros Maroc........................ Curve = Conductivity + 1·5
△ Barbarossa........................ Curve = Conductivity + 3·0
★ Waltham Cross........................ Curve = Conductivity + 4·5
● Flaming Tokai........................ Curve = Conductivity + 4·5]

The values are in close agreement, but the method is a difficult one to apply in practice since the colours are difficult to judge correctly and small changes in $_pH$ are accompanied by relatively large changes in the acid-content of the juice. This is particularly true as the grapes approach maturity.

The curve obtained for the changes in the conductivity of the juice was very similar to that for acidity (see Curve III). This similarity seems to indicate that the conductivity is mainly due to the presence of the free acid in the juice. Since other workers * have shown that the cream of tartar increases only slightly



CURVE IV.—ASTRINGENCY AS GRAMMES TANNIN PER 100 C.C. JUICE.

+ White Hanepoot.
× Red Hanepoot........................... Curve = Tannin + 0·02
○ Gros Maroc........................... Curve = Tannin + 0·04
△ Barbarossa........................... Curve = Tannin + 0·06
★ Waltham Cross........................... Curve = Tannin + 0·02
● Flaming Tokai........................... Curve = Tannin + 0·06

during ripening, this *decrease* in the conductivity would indicate that there was an actual disappearance of acid during the ripening process. In following the changes in acid-content the simplest method in practice would seem to be the titration method, and it yields results of greater accuracy with less trouble.

The data obtained for the "soluble solids" in the juice showed close agreement with the Balling degrees of the juice and indicate clearly the significance to be attached to the Balling reading. The changes in the "soluble

* Bioletti Cruess and Davi. Univ. of Calif. Pubs. in Agr. Sc. Vol. 3, No. 6. 1918. Lewis. Bull., Dept. of Agric. No. 69, 1910.

solids" have, therefore, not been shown by means of a curve, and the same description applies to them as to the curve for the Balling degrees. As the grapes ripen, the differences between these two readings and the sugar-content of the juice becomes less and at maturity becomes fairly constant. In the initial stages of ripening the high difference is, no doubt, due to the high acid-content of the unripe grapes. The fact that at maturity the difference remains fairly constant is to be expected since the cream of tartar, acid, and protein remain fairly constant as maturity is reached. At maturity there was a general difference of 0·8–1·2 between the Balling reading and the sugar-content *per* 100 *c.c.* In this way, by subtraction, a close approximation to the sugar-content may be obtained. This figure agrees with that obtained by Bioletti, Cruess, and Davi * for American grapes.

It would appear that as the grape ripens, the decrease in "non-sugar soluble solids" is mainly due to the disappearance of acid. At the same time their conversion into sugar would *not* explain the rapid increase in sugar-content.

The calculation of the astringency in terms of the factor for tannin involves a considerable error since the astringent non-tannins are highly diverse in character. The figures obtained are not absolute but are serviceable for purposes of comparison. In the initial stages of ripening there was a general tendency for this factor to decrease, but during ripening and during maturity the variations of astringency were very irregular. The deeply coloured varieties tended to show a slightly higher value than the remaining varieties. These changes have been shown by means of a curve (see Curve IV), but, owing to the limitations of the method, no attempt has been made to draw a smooth curve. These conclusions agree with those found by Noyes, King, and Martsolf for the Concord † grape. The value of the astrigency varied between 0·04 and 0·07 gramme per 100 c.c. at maturity according to the variety of grape.

The date for the determinations made upon the whole berry have been included in Tables XI to XVI, in which have been included the values for the ratios which have been found most important in determining the equilibrium of the various factors at maturity.

TABLE XI.—WHITE HANEPOOT.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/ Solids.	Ratio Sugar/ Solids.	Ratio. Acid × 10/Sugar.
13/1/26	7·88	·32	·063	4·02	·20	20·94
20/1/26	8·72	·26	·062	2·93	·42	8·83
27/1/26	10·86	·33	·061	3·06	·73	2·84
3/2/26	12·84	·43	·059	3·36	·78	1·90
10/2/26	13·73	·38	·057	2·74	·79	1·50
17/2/26	16·81	·40	·054	2·40	·88	0·68
24/2/26	18·30	·42	·048	2·28	·91	0·54
3/3/26	20·53	·44	·061	2·12	·88	·43
10/3/26	24·04	·47	·067	1·98	·90	·32
17/3/26	23·36	·50	·069	2·14	·85	·32
24/3/26	23·28	·54	·069	2·32	·93	·28

* Bioletti, Cruess, and Davi, *loc. cit.*

† J.A.O.A.C. Vol. 6, No. 2. 1922.

TABLE XII.—RED HANEPOOT.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/Solids.	Ratio Sugar/Solids.	Ratio Acid × 10/Sugar.
13/1/26	8·00	·32	·060	3·98	·19	21·30
20/1/26	9·58	·29	·061	3·02	·29	12·00
27/1/26	10·79	·37	·055	3·40	·71	3·23
3/2/26	13·35	·45	·051	3·36	·79	1·72
10/2/26	16·02	·44	·048	2·78	·74	1·44
17/2/26	16·90	·42	·045	2·47	·87	·75
24/2/26	18·95	·42	·044	2·21	·89	·60
3/3/26	21·16	·44	·066	2·07	·90	·38
10/3/26	22·06	·52	·073	2·38	·89	·37
17/3/26	21·94	·49	·054	2·24	·84	·35
24/3/26	23·54	·56	—	2·38	·89	·25

TABLE XIII.—GROS MAROC.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/Solids.	Ratio Sugar/Solids.	Ratio. Acid × 10/Sugar.
13/1/26	8·46	·33	·068	3·90	·16	27·58
20/1/26	7·91	·28	·069	3·58	·17	26·87
27/1/26	8·89	·31	·064	3·53	·20	20·20
3/2/26	10·04	·28	·069	2·79	·32	11·21
10/2/26	13·38	·31	·070	2·29	·49	4·26
17/2/26	15·99	·31	·063	1·93	·54	2·63
24/2/26	17·39	·36	·054	2·08	·73	1·33
3/3/26	17·90	·37	·078	2·07	·75	1·16
10/3/26	19·32	·38	·062	1·99	·74	·74
17/3/26	19·86	·43	·058	2·17	·80	·71
24/3/26	19·68	·42	·069	2·14	·78	·70

TABLE XIV.—BARBAROSSA.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/Solids.	Ratio Sugar/Solids.	Ratio Acid × 10/Sugar.
13/1/26	8·98	·34	·072	3·75	·16	21·10
20/1/26	9·37	·31	·069	3·31	·19	16·86
27/1/26	9·13	·30	·074	3·32	·19	18·55
3/2/26	11·22	·35	·062	3·12	·37	6·31
10/2/26	12·20	·36	·055	2·98	·76	2·07
17/2/26	14·53	·33	·053	2·28	·77	1·38
24/2/26	18·04	·39	·045	2·15	·77	·87
3/3/26	19·03	·42	·053	2·22	·78	·73
10/3/26	20·16	·44	·062	2·19	·82	·58
17/3/26	22·13	·47	·052	2·30	·79	·52

TABLE XV.—WALTHAM CROSS.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/ Solids.	Ratio Sugar/ Solids.	Ratio Acid × 10/Sugar.
13/1/26	9·97	·42	·060	4·24	·49	5·79
20/1/26	10·46	·34	·057	3·22	·50	4·86
27/1/26	12·55	·33	·062	2·63	·63	2·54
3/2/26	13·04	·36	·059	2·73	·76	1·51
10/2/26	15·66	·42	·057	2·68	·84	·95
17/2/26	15·50	·44	·055	2·83	·82	·95
24/2/26	16·86	·45	·054	2·67	·85	·69
3/3/26	20·43	·47	·073	2·31	·88	·45
10/3/26	—	—	·070	—	—	·37

TABLE XVI.—FLAMING TOKAI.

Date.	Per Cent. Total Solids in Berry.	Per Cent. Ash in Berry.	Per Cent. Total Nitrogen in Berry.	Ratio Ash/ Solids.	Ratio Sugar/ Solids.	Ratio Acid × 10/Sugar.
13/1/26	8·91	·31	·079	3·52	·10	36·60
20/1/26	9·27	·33	·063	3·59	·13	30·07
27/1/26	10·48	·38	·074	3·60	·31	11·02
3/2/26	10·67	·35	·084	3·30	·46	6·90
10/2/26	11·79	·38	·076	3·21	·61	3·73
17/2/26	14·76	·42	·067	2·82	·60	2·38
24/2/26	17·69	·44	·055	2·47	·71	1·17
3/3/26	18·27	·46	·067	2·52	·80	·78
10/3/26	21·07	·50	·067	2·38	·76	·61
17/3/26	19·69	·44	·066	2·41	·79	·55
24/3/26	21·05	·53	—	2·50	·80	·47

The changes in the " total solids in the berry " follow closely the changes in the Balling reading, and as similar remarks apply to them no attempt has been made to show these changes by means of curves. They resembled the changes which occurred in 1925 except that the initial period, prior to " veraison," and the more prolonged period of maturity were more evident in the present work. It may be concluded that for maturity the value must be at least that given in Table XIII.

TABLE XIII.—TOTAL SOLIDS IN BERRY.

	1926.	1925.
White Hanepoot	21·5	21·0
Red Hanepoot	21·0	21·0
Gros Maroc	18·0	18·5
Barbarossa	19·0	18·5
Waltham Cross	16·8	18·0
Flaming Tokai	20·0	20·0

The values are in close agreement and indicate that there is a definite concentration of solids in the berry when maturity is reached. In the present case this value was reached about the end of the first week in March, except in the case of Waltham Cross, where this stage was reached about the middle of February. The close similarity between the rates at which the total solids of the berry and the sugar-content of the juice increase indicate that the increase in the former is mainly due to increases in the latter.

The proportion of ash in the berry showed initially a slight decrease, indicating a more rapid production of organic matter in the berry. During the period of ripening, however, the ash slowly increased until, at maturity, the amount was about 0·5 per cent. This value differed but little for the various varieties, but is slightly higher than that obtained by Lewis * and Frater † for ripe wine grapes. The very slow increase in ash-content during ripening would seem to be closely connected with the production of cream of tartar. The ratio of ash to total solids showed that the proportion of ash tended to decrease to a minimum value, which changed only slightly at maturity. The value varied slightly for each variety of grape between 2·0 and 2·5, the firmer varieties having a slightly higher value than the softer varieties. It would appear that the mineral-content of the grapes is connected with their texture. These results are in close agreement with those for 1925.

The changes in nitrogen-content indicated that there was a slow decrease during the period of ripening until maturity was reached, when there was a sudden increase. It would appear that the production of sugar is more rapid than the production of nitrogenous substances, and that the processes of ripening are not greatly dependent upon the content of nitrogen. The subsequent increase of nitrogen to a practically maximum value occurred at slightly differing periods according to the variety of grape. This maximum value varied from 0·060 to about 0·080 per cent, which is in close agreement with the values obtained in 1925.

In dealing with the results as a whole, the fact that the factors tend to reach a limiting value at maturity becomes clear, and, therefore, some equilibrium must be set up which is not subject to any very great change during this period. Since the most important factors are the sugar and acid-content these have been employed in attempting to determine this relationship.

As already mentioned, the errors involved in determining the yield of juice are large, and, therefore, no attempt has been made to calculate the yield of sugar from a given weight of berries. For this reason the purely arbitrary ratio of sugar per 100 c.c. juice to " total solids in the berry " has been calculated. The ration of acid to sugar has also been determined.

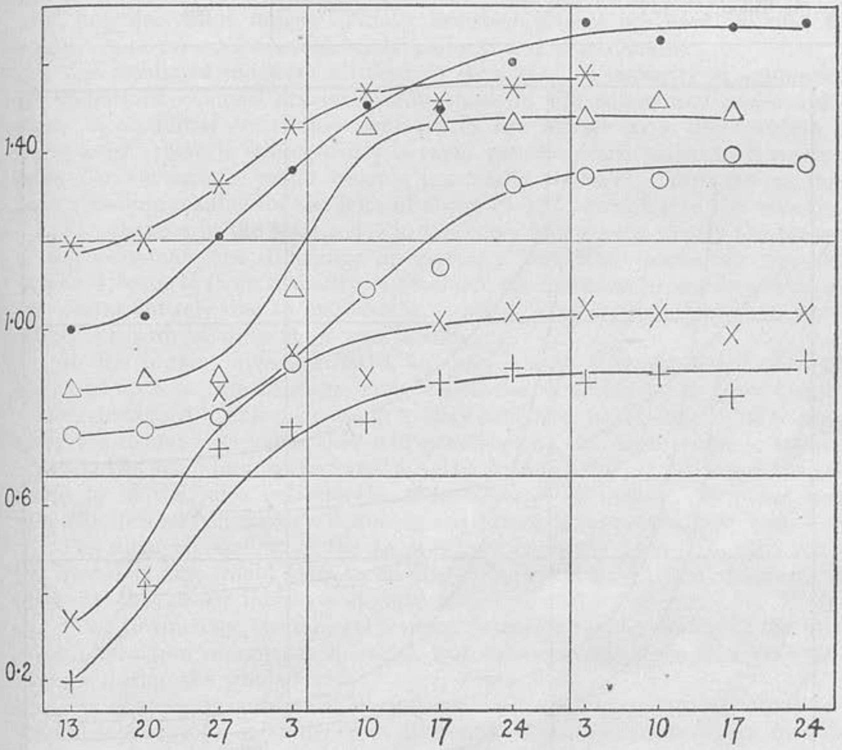
On examining the curve for the first ratio it is clear that when maturity is reached a definite relationship was set up between the total solids of the berry and the sugar-content of the juice. The value increased to a maximum which varied slightly for each variety, but lay between 0·80 and 0·90. (See Curve V.) The value thus given is an arbitrary figure and does not actually indicate the proportion of sugar in the berry since no correction has been made for the proportion of juice in the berry. However, it showed clearly that at maturity there was a constant relationship between these two factors, and, therefore, the increases in solids are mainly due to the production of sugar.

The curve showing the changes in the ratio of acid to sugar followed very closely the curve for the previous seasons. (See Curve VI.) There was initially a very rapid decrease, which gradually became less until at maturity

* Lewis, Bull., Dept of Agr. 69, 1910.

† Frater, Bull., Dept. of Agr., Div. of Chem. Series No. 32, 1925.

a practically constant minimum value was obtained. This fact shows that when the grape has ripened, the changes which take place in these two important factors are small, and that there is definite relationship between the sugar, and acid-content of the juice. Noyes, King, and Martsolf * state in their paper that "with certain reservations, sugar should increase and acid diminish as longs as the leaves function properly. This, however, is not always the case, for, as soon as the pedicles begin to wither, the fruit is gradually cut off from further influence of the growth processes taking place in the plant, and its sugar-content may remain fairly constant for some time." Evaporation of water from the



CURVE V.—RATIO—SUGAR PER 100 C.C. JUICE/TOTAL SOLIDS PER 100 GRAMMES BERRY.

+ White Hanepoot.
× Red Hanepoot.......................... Curve = Ratio + 0·15
○ Gros Maroc.......................... Curve = Ratio + 0·60
△ Barbarossa.......................... Curve = Ratio + 0·70
★ Waltham Cross.......................... Curve = Ratio + 0·70
● Flaming Tokai.......................... Curve = Ratio + 0·90

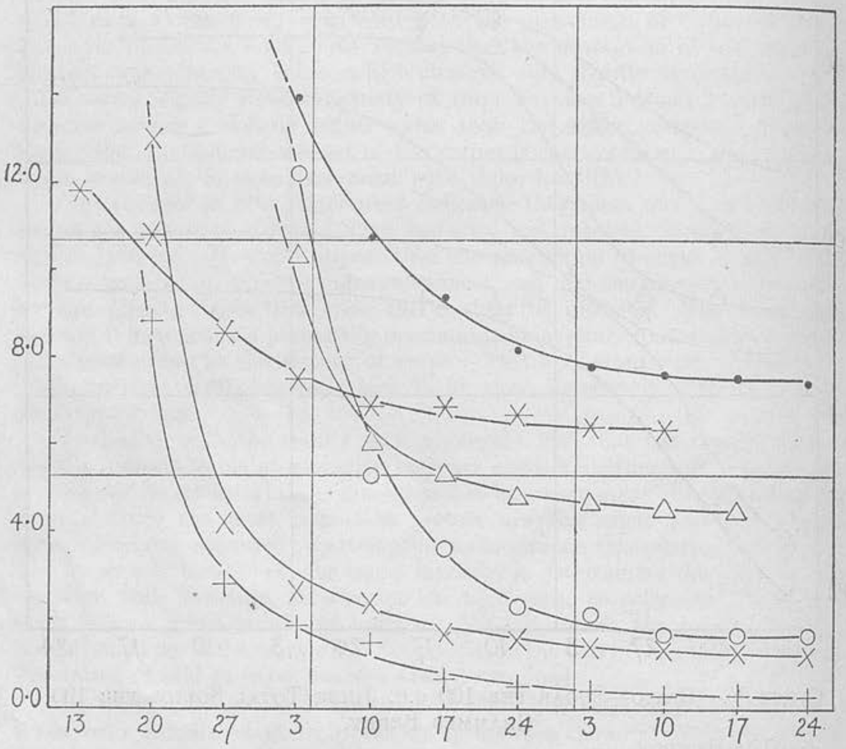
berries and the respiratory processes of the fruit *may* appear to cause slight variations in either direction.

This ratio, then, may give important information regarding the ripeness of the fruit. The limiting value varies according to the variety of grape, and, in the present case, for a ripe grape the value was, at most, that given in Table XVII in which the values from previous years are included for comparison.

* "Variations in Concord Grape during Ripening," J.A.O.A.C., Vol. 6, No. 2, 1922.

TABLE XVII.—RATIO ACID × 10/SUGAR.

	1926.	1925.	1923.
White Hanepoot	·37	·36	·30
Red Hanepoot	·36	·36	·30
Gros Maroc	·70	·52	—
Barbarossa	·55	·40	·38
Waltham Cross	·40	·38	—
Flaming Tokai	·55	·40	·36



CURVE VI.—RATIO—ACIDITY × 10/SUGAR.

+ White Hanepoot.
× Red Hanepoot.......... Curve = Ratio + 1·0
○ Gros Maroc.......... Curve = Ratio + 1·0
△ Barbarossa.......... Curve = Ratio + 4·0
★ Waltham Cross.......... Curve = Ratio + 6·0
● Flaming Tokai.......... Curve = Ratio + 7·0

These values agree very well, being only slightly higher than in previous years. White Hanepoot, Red Hanepoot, and Waltham Cross, grapes with a sweet flavour, showed lower values than the remaining varieties with a tart flavour.

Summary.

The present work confirms the results of the previous investigations. Although the data are not so extensive, the changes have been studied more fully by lengthening the period of investigation so that the initial and final changes were more clearly defined.

During the present investigation the grapes matured slightly later than previous years, but the data obtained for ripe grapes are in close agreement, showing clearly that some definite relationship exists between the various factors at maturity.

It has been found that data upon the yield of juice and of residue are of little practical value unless specially designed presses are used, so that the conditions of pressing are absolutely uniform and reproducable.

The results of the work all tend to show that as maturity is approached the important changes are essentially those in the sugar- and acid-content. There is an initial very slow increase in the former to a stage known as "veraison," there is subsequently a rapid increase until maturity is reached, when the amounts of sugar become practically constant. Ripe grapes must have a Balling reading for the juice of about 16–19°, according to the variety.

The changes in the total solids in the berry follow very closely the changes in sugar-content, the difference at maturity becoming practically constant. It would seem that as maturity is attained, the increases in solid-content are are almost entirely due to increases in sugar-content, so that finally an equilibrium is set up between these two factors.

In the present investigation it has been shown that the acidity initially increases up to a certain stage, after which the berry begins to ripen and the acidity decreases. This decrease in acidity continues until maturity is reached, when the decrease becomes slow and practically a minimum value is reached, which varies according to the variety. The data for the $_{p}H$ value and the conductivity of the juice indicate the same changes in acidity. It would seem that the decrease in acidity is due to the actual disappearance of acid.

The nitrogen-content of the berry decreases slowly during the ripening of the fruit, and this would seem to be due to the rapid production of sugar. At maturity this factor increases slightly.

Prior to ripening, the mineral-content decreases slightly owing to the more rapid production of organic material, but subsequently there is a very slow increase during the whole period.

The changes in astringent matter are somewhat irregular, but there is a general tendency for it to decrease during the ripening in accordance with the development of the milder flavour of the ripe fruit.

The relationships between the acid, sugar, and solids indicate that a definite equilibrium is set up at maturity, and the question of applying these facts to the determination of the ripeness of the grape will be dealt with in a later paper.

The author of this paper wishes to thank Mr. R. B. Borcherds, B.A., for his assistance in carrying out a portion of the analytical work in connexion with this paper.

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SOME PHYSICAL AND CHEMICAL CHANGES OCCURRING DURING THE RIPENING OF GRAPES

(SECOND PAPER)

BY

P. R. v. d. R. COPEMAN, B.A., B.Sc. D.Sc. 1928

AND

G. FRATER, B.A.

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SOME PHYSICAL AND CHEMICAL CHANGES OCCURRING DURING THE RIPENING OF GRAPES.

(SECOND PAPER.)

By P. R. v. d. R. COPEMAN, B.A., B.Sc., and G. FRATER, B.A.

SOME previous work* in connexion with the physical and chemical changes which occur during the ripening of grapes had indicated that further investigation would be of interest and importance from the point of view of the factors that determine the condition of ripeness in a grape.

The reasons which led to the undertaking of this particular investigation have been given in the bulletin referred to above, in which also a brief summary was given of work along similar lines carried out by previous workers. During the publication of the first investigation another paper† dealing with the composition of ripe wine grapes appeared, and some of the analytical methods have been adopted in the present investigation. In this latter bulletin a fairly complete set of references has been given dealing with the questions of the composition of the grape. The present investigation may therefore be regarded as an amplification of work carried out in 1923.

Six varieties of table grapes were studied, namely, White Hanepoot, Red Hanepoot, Barbarossa, Flaming Tokai, Waltham Cross, and Gros Maroc, of which the first four varieties had been employed in the previous investigation. The samples were all obtained from the Government Wine Farm, Groot Constantia, but in this case, in order that the work should not be limited by the facilities available, the analytical determinations were carried out in the Government Laboratories, Capetown. Through the kindness of the manager of the farm the supplies were sent regularly once a week to the laboratory from 28th January to 11th March, 1925. On account of the early completion of the vintage, the determinations were not prolonged sufficiently to afford a comparison with the final two weeks of the 1923 investigation. The grapes were picked in the early morning, and the analysis commenced immediately on arrival at the laboratory, probably about three hours after picking.

However, working under these conditions, determinations could be made with greater care and accuracy. All the quantities, previously determined, were repeated and the reasons for choosing such data have already been outlined in the first bulletin, but owing to greater facilities the following quantities were also determined:—Total soluble nitrogen and ammoniacal nitrogen in the juice, total nitrogen in the berry, ash in the berry, percentage of seeds in the berry, total solids, and ash in the seeds.

* Copeman: Dept. of Agr. Bull., Division of Chem. Series No. 31.
† Frater: Dept. of Agr. Bull., Division of Chem. Series No. 33.

At present there is no method of measuring quantitatively all the elements which enter into a determination of the ripeness of a fruit. Not only are sugars and acids concerned, but the texture, aroma, and minute quantities of flavouring substances are also involved. In the case of plums it has been found* that sugar-content is closely associated with other constituents that determine this quality and is therefore a measure of this quality. Since in all fruits the characteristic of taste depends principally upon the sugars and acids, it seems probable that the same conclusion should be applicable, particularly to a fruit like the grape where the greater portion of the total solids consists of sugar. Naturally enough variations will depend upon conditions such as climate, soil, and aspect of the vineyard, but these should not be sufficiently great to vitiate the general argument. The 1925 season was again remarkable for the fact that, in no case, did rain interfere with the picking and sampling of the grapes.

Ten bunches of each variety of grape on arrival at the laboratory were weighed, and from these ten bunches average samples of the berries were obtained as required.

The average weight and average volume of the berry were determined as outlined in the previous work. In the present instance, the juice from 100 berries was expressed by means of a small fruit-press, collected in a porcelain dish and filtered through coarse linen into a measuring cylinder for the determination of the volume. The reading of the Balling hydrometer and the temperature were noted, while the density of the juice was determined by means of a Westphal balance. These two readings were corrected to 20° C. by means of tables.

The total acidity was determined as before, but the $_{p}H$ value (hydrogen-ion concentration) of the juice was determined electrically. The apparatus used was the Gallenkamp electrometric apparatus with a saturated calomel electrode. In this way the colour and turbidity of the juice was eliminated as a source of error, and the method is more accurate than the colorimetric method. The method is a potentiometer one and the $_{p}H$ value is calculated from the potential difference between the hydrogen electrode and the juice.

The method of determining the sugar-content was completely altered and the method of Lane and Enyon† adopted, in which methylene blue was used as an internal indicator with Fehling's solution. This was found to be entirely satisfactory. 50 c.c. of the juice was diluted, clarified with 10 c.c. of saturated lead acetate and the whole made up to 250 c.c. After settling, 50 c.c. of the clear supernatant liquid was pipetted into a 200 c.c. measuring flask, 10 c.c. of 20 per cent. potassium oxalate added and the whole made up to the mark. The liquid was filtered and 50 c.c. of the clear solution made up to 150 c.c. for the final titration. To a second 50 c.c. portion 10 c.c. of 10 per cent. H.Cl. were added and the flask heated on the water-bath to complete inversion. The liquid was cooled, neutralized with caustic soda, using litmus paper, and then made up to 150 c.c. This solution was used for the determination of sucrose, if any were present.

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* Diehl and Magness: Monthly Bull. of Dept. Agr., Calif., Vol. XI, No. 4, 1922, p. 387.

† Lane and Enyon, *J.S.C.I.*, 1923, p. 32 T.

The "permanganate value" was determined and calculated as before. It is important that sufficient excess of conc. sulphuric acid be added.

The loss of weight and total solids, both of the berries and of the seeds, were determined after crushing them in a porcelain dish and heating in a water-oven until a constant weight was obtained. The results were calculated as percentages. The residue was then ignited at a low red heat in order to determine the ash both of the berries and of the seeds. It is important that the temperature of ignition be kept as low as possible so that no volatilization occurs. This was accomplished by preventing any fusion of the ash, and in every case a clean greyish white ash was obtained. The percentage of seeds was obtained by removing the seeds from 25 weighed berries, freeing them from adhering pulp, drying between filter paper, and then weighing.

The determinations of nitrogen in juice and in berry were carried out according to the standard Kjeldahl method. 25 c.c. of juice was used for the determination of total soluble nitrogen and 100 c.c. for the determination of ammoniacal nitrogen. For the latter, freshly ignited magnesium oxide was used. Whole berries were used for the determination of total nitrogen in the berry.

On account of the large number of determinations the results have been divided into sections and will be discussed in the following order:—

A. Physical properties of the berry.
B. Chemical composition of the juice.
C. Analyses of the berry.
D. Analyses of the seeds.
E. Some equilibrium relationships.
F. Summary and conclusions.

In order that the analytical data may be more readily studied and the changes made more apparent, the results in all cases have also been presented in the form of curves. Owing to the almost insuperable difficulties of obtaining absolutely representative samples from a product so widely variable as a fruit, it would not be expected that the analytical data would fall completely on a smooth curve. However, in order to simplify the data and render the changes more clear, it has been decided to draw smooth curves, and to regard irregularities as experimental errors. The curves, so obtained, probably represent, with some degree of accuracy, the changes which occur during the ripening of the fruit. In this connexion some remarks in a paper * by Bioletti, Cruess, and Davi are particularly significant. They point out that considerable irregularity occurs in the samples from week to week. They show that young vines ripen their fruit earlier than mature vines. Therefore samples should be taken from vines of the same age. The position of the bunch on the vine affects the composition of the fruit. The bunches on the side of the vine most exposed to the sun and the bunches near the tip of the vine ripen more rapidly than those on the shady side and lower down on the vine. Even when these factors are taken into account there is still some variation in the Balling degree of the juice from bunches of similar appearance and size, from the same vineyard on the same date. In addition to this the position of the berries on the bunch affects the composition of the fruit. However, degree of pressing

* Bioletti, Cruess, and Davi: Univ. of Calif. Pubs. in Agr. Sc., Vol. III, No. 6, 1918.

appeared to have no effect upon the analytical results. These facts show how difficult it is to select grapes which will represent an average sample. Therefore we may regard the smooth curves as an approximation which is justified by the difficulties involved.

TABLE I.
White Hanepoot.

Date.	Average Weight of Bunch in grms.	Average Weight of Berry in grms.	Average Volume of Berry in c.c.	Density of Berry.	Volume of Juice in c.c. from 100 Berries.	Yield of Juice in c.c. from 100 grms. of Berry.
28.1.25..........	294·5	3·53	3·40	1·039	166	47·0
4.2.25..........	286·5	4·51	4·04	1·116	220	48·8
11.2.25..........	305·0	4·66	4·26	1·094	271	58·2
18.2.25..........	303·1	5·11	4·65	1·098	345	67·5
25.2.25..........	445·5	5·82	5·40	1·078	380	67·5
4.3.25..........	319·9	5·93	5·47	1·084	413	68·9
11.3.25..........	275·9	6·12	5·75	1·064	424	65·9

TABLE II.
Red Hanepoot.

28.1.25..........	210·2	3·10	3·00	1·033	149	48·1
4.2.25..........	229·0	3·72	3·50	1·063	198	53·2
11.2.25..........	288·7	4·62	4·26	1·085	281	60·8
18.2.25..........	299·0	5·28	4·96	1·065	369	70·0
25.2.25..........	372·3	5·74	5·52	1·040	405	70·6
4.3.25..........	190·4	5·76	5·48	1·051	394	68·5
11.3.25..........	371·0	6·30	6·00	1·050	436	69·3

TABLE III.
Gros Maroc.

28.1.25..........	183·3	2·73	2·62	1·043	168	61·5
4.2.25..........	184·5	3·52	3·29	1·070	218	61·9
11.2.25..........	203·5	4·21	3·90	1·080	300	67·6
18.2.25..........	243·7	4·59	4·30	1·068	330	71·6
25.2.25..........	220·8	4·51	4·38	1·034	329	72·9
4.3.25..........	236·0	4·92	4·59	1·071	346	70·3
11.3.25..........	251·5	5·15	4·80	1·071	362	70·3

TABLE IV.
Barbarossa.

28.1.25..........	197·7	2·03	1·95	1·041	120	59·1
4.2.25..........	297·5	2·65	2·50	1·060	160	60·4
11.2.25..........	232·3	2·75	2·65	1·038	195	70·9
18.2.25..........	225·8	3·42	3·22	1·054	257	74·8
25.2.25..........	371·5	3·99	3·74	1·051	302	75·0
4.3.25..........	463·3	4·60	4·35	1·057	355	73·4
11.3.25..........	455·4	4·90	4·62	1·060	373	72·8

TABLE V.
Waltham Cross.

Date.	Average Weight of Bunch in grms.	Average Weight of Berry in grms.	Average Volume of Berry in c.c.	Density of Berry.	Volume of Juice in c.c. from 100 Berries.	Yield of Juice in c.c. from 100 grms. of Berry.
28.1.25..........	340·0	3·80	3·75	1·014	210	55·3
4.2.25..........	292·5	3·94	3·79	1·040	245	62·2
11.2.25..........	281·7	4·02	3·85	1·045	260	64·7
18.2.25..........	254·0	5·29	5·03	1·052	396	74·8
25.2.25..........	232·5	5·80	5·48	1·059	427	73·6
4.3.25..........	289·5	6·34	6·04	1·049	476	74·1
11.3.25..........	333·2	6·65	6·40	1·037	516	74·3

TABLE VI.
Flaming Tokai.

28.1.25..........	322·5	3·55	3·43	1·034	180	50·7
4.2.25..........	414·8	4·04	3·89	1·039	228	56·4
11.2.25..........	401·7	5·21	4·80	1·084	348	66·8
18.2.25..........	399·7	5·68	5·34	1·064	417	73·4
25.2.25..........	395·8	6·58	6·18	1·065	491	74·7
4.3.25..........	405·0	6·52	6·14	1·062	477	73·1
11.3.25..........	450·0	6·80	6·36	1·070	506	72·5

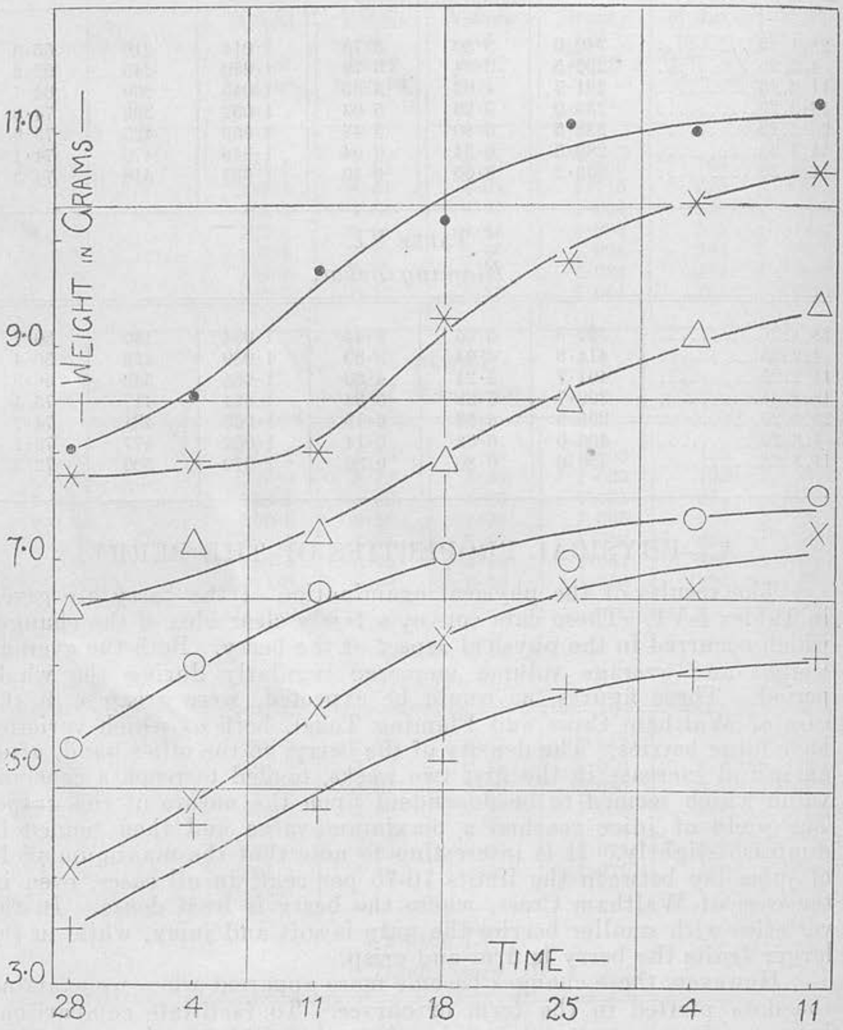
A.—PHYSICAL PROPERTIES OF THE BERRY.

The results of the physical examination of the berry are given in Tables I-VI. These data convey a fairly clear idea of the changes which occurred in the physical aspect of the berry. Both the average weight and average volume increased regularly during the whole period. These figures, as would be expected, were greatest in the case of Waltham Cross and Flaming Tokai, both of which varieties have large berries. The density of the berry, on the other hand, after an initial increase in the first two weeks, tended to reach a constant value which seemed to be dependent upon the nature of the grape. The yield of juice reached a maximum value and then tended to diminish slightly. It is interesting to note that the maximum yield of juice lay between the limits 70-75 per cent. in all cases, even in the case of Waltham Cross, where the berry is least dense. In the varieties with smaller berries the pulp is soft and juicy, while in the larger fruits the berry is firm and crisp.

However, these changes become more apparent when we examine the data plotted in the form of curves. To facilitate comparisons between the curves, each set has been grouped together and each individual curve separated from its neighbour by suitable additions, which are shown below each curve.

AVERAGE WEIGHT OF BERRY.

The curves all showed the same general characteristics. Initially, the weight increased rapidly, but finally the increase in weight diminished until, at the end of the period under review, the weight had reached practically a maximum value. This period of maximum weight agrees well with that found in the 1923 investigation and it may be concluded that the berries had reached their maximum growth about 4th-11th March. After this period the berry begins to be cut off from the processes of growth in the plant, and little further increase in size can be expected.

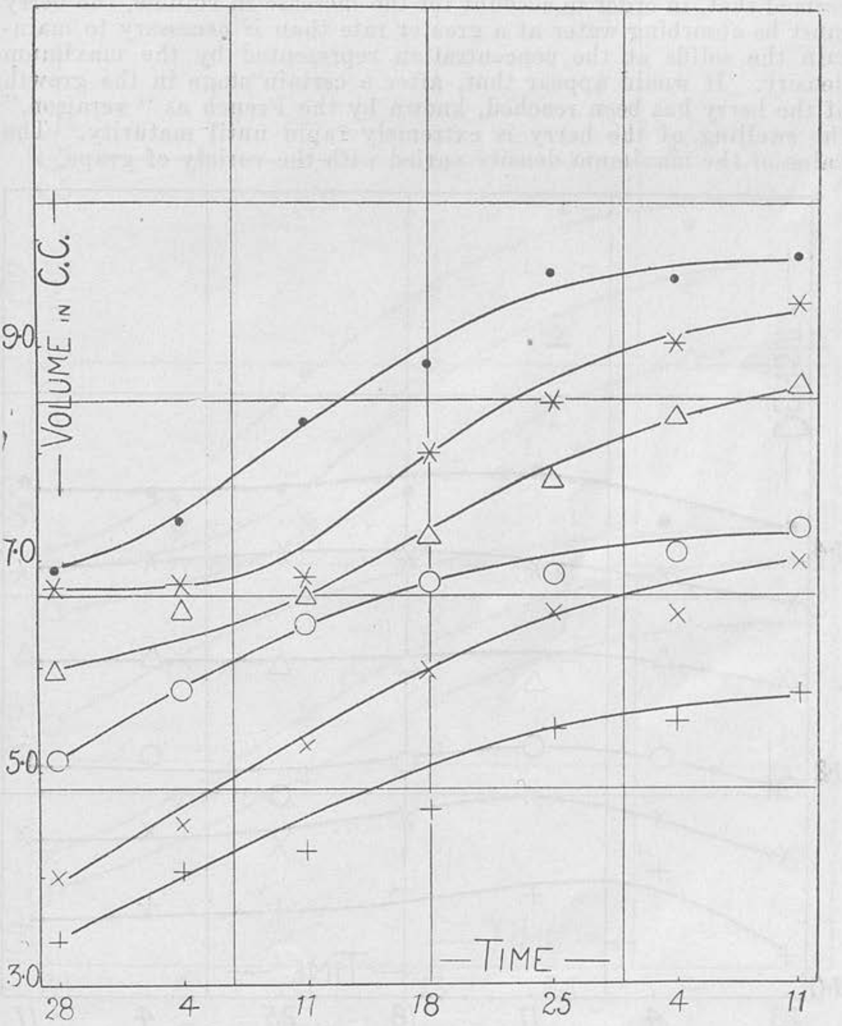


CURVE 1.—AVERAGE WEIGHT OF BERRY.

+ White Hanepoot.
× Red Hanepoot. Curve = Weight + 1·0.
○ Gros Maroc. Curve = Weight + 2·5.
△ Barbarossa. Curve = Weight + 4·5.
✱ Waltham Cross. Curve = Weight + 4·0.
● Flaming Tokai. Curve = Weight + 4·5.

Average Volume of Berry.

The changes in volume of the berry followed very closely the changes in weight, the maximum value being reached at the same period. On account of the early curtailment of the present investigation, the phenomenon of shrinking has not become apparent. When the grapes become fully mature the berry ceases to increase in size.

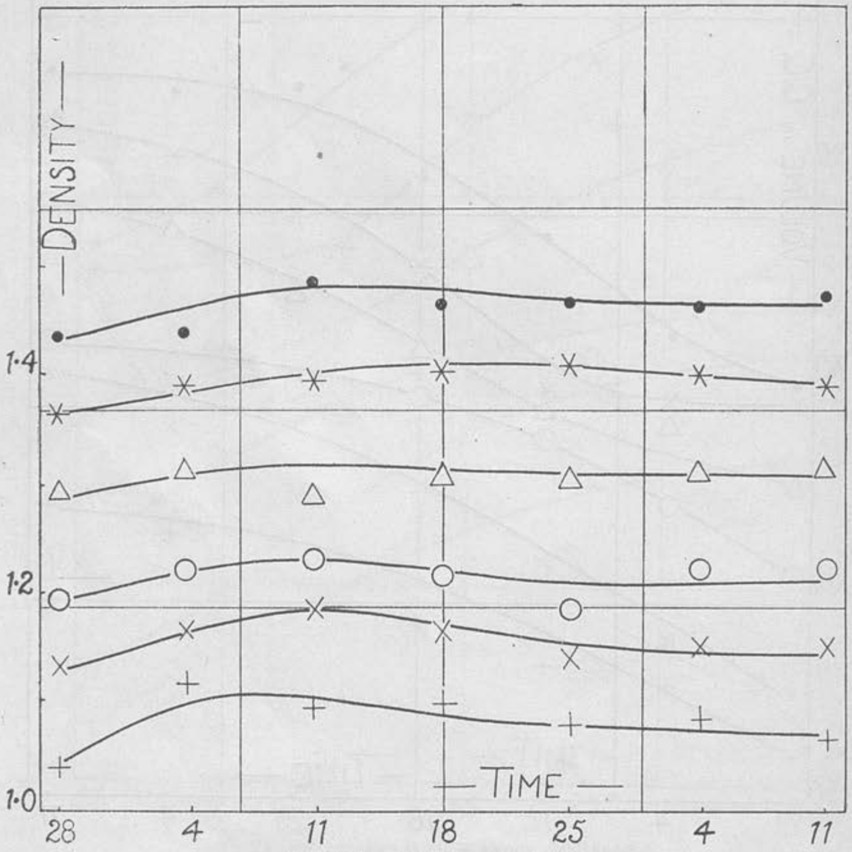


Curve 2.—Average Volume of Berry.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Volume + 1·0.
○ Gros Maroc.	Curve = Volume + 2·5.
△ Barbarossa.	Curve = Volume + 4·0.
* Waltham Cross.	Curve = Volume + 3·0.
● Flaming Tokai.	Curve = Volume + 3·5.

Density of Berry.

There was an initial increase in the density due probably to a very rapid accumulation of the products of growth in the berry. In all cases a point of maximum density was reached, after which the value remained practically constant or even decreased slightly. Initially, the accumulation of products was more rapid than could be compensated for by the natural increase in volume, but finally such compensation occurred. Where the density decreased slightly it seemed that, in order to account for the increase in volume, the berry must be absorbing water at a greater rate than is necessary to maintain the solids at the concentration represented by the maximum density. It would appear that, after a certain stage in the growth of the berry has been reached, known by the French as "veraison," the swelling of the berry is extremely rapid until maturity. The value of the maximum density varied with the variety of grape.

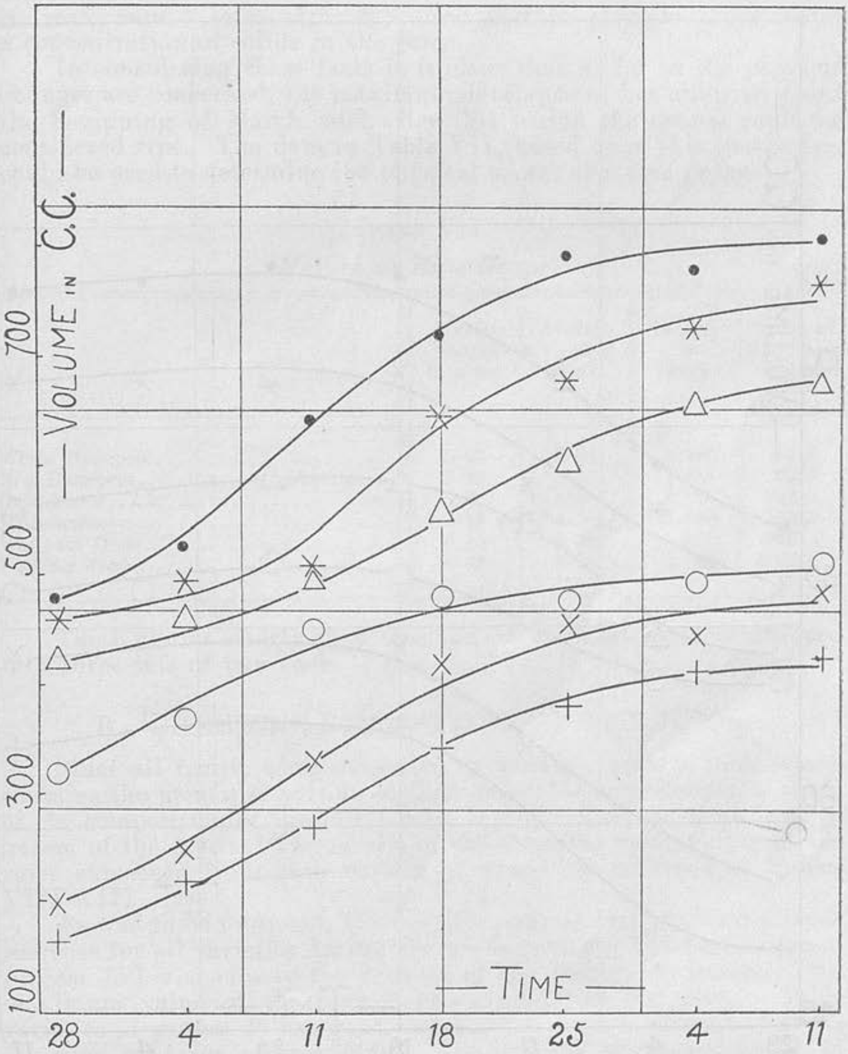


Curve 3.—Density of Berry.

+ White Hanepoot.
× Red Hanepoot. Curve = Density + 0·10.
○ Gros Maroc. Curve = Density + 0·15.
△ Barbarossa. Curve = Density + 0·25.
* Waltham Cross. Curve = Density + 0·35.
● Flaming Tokai. Curve = Density + 0·40.

VOLUME OF JUICE.

The curves all increased, at first rapidly and finally more slowly, until practically a maximum value was reached. It is significant that the final values are such that the six varieties may be grouped into three sets of two: (*a*) Gros Maroc and Barbarossa with small soft berries gave practically the same volume of juice per 100



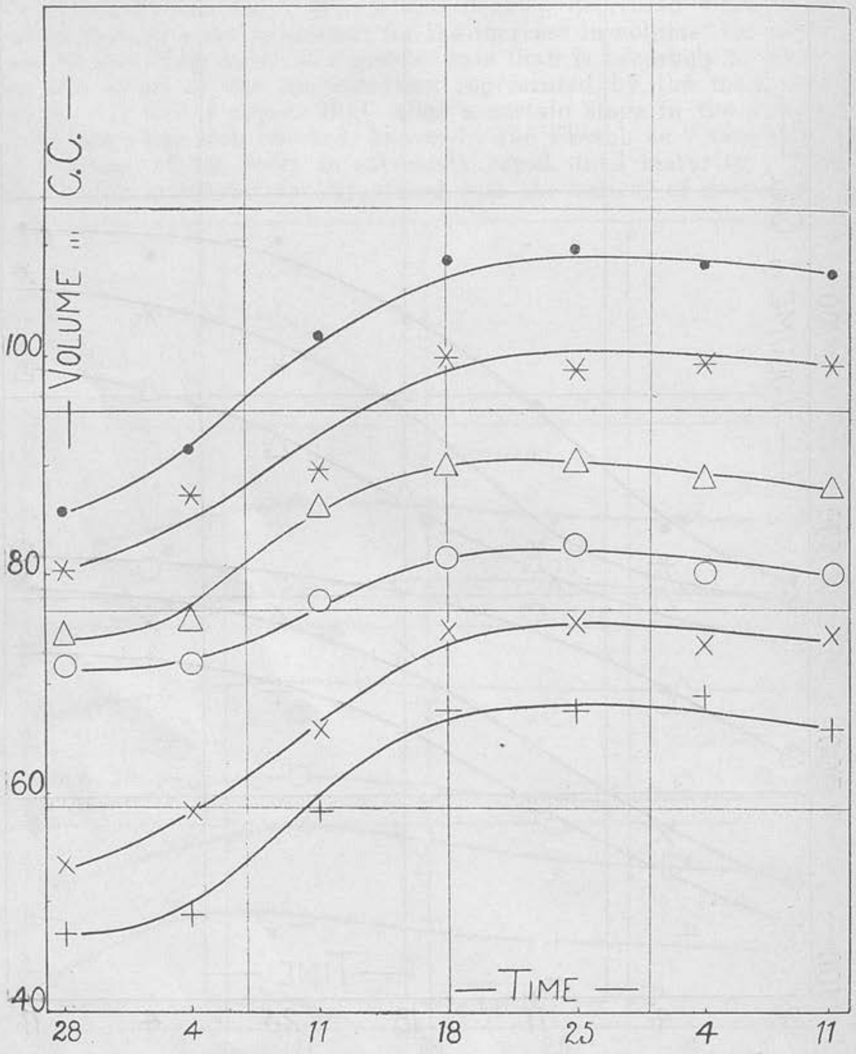
CURVE 4.—VOLUME OF JUICE FROM 100 BERRIES.

+ White Hanepoot.
× Red Hanepoot. Curve = Volume + 50.
○ Gros Maroc. Curve = Volume + 150.
△ Barbarossa. Curve = Volume + 300.
* Waltham Cross. Curve = Volume + 250.
● Flaming Tokai. Curve = Volume + 300.

berries (and the smallest volume); (*b*) White Hanepoot and Red Hanepoot yielded the same volume; (*c*) finally, Waltham Cross and Flaming Tokai, both with large fleshy berries, gave almost identical as well as largest volumes of juice.

YIELD OF JUICE PER 100 GRMS.

In every case this value increased to a maximum and then decreased, and again the curves show that the same groupings of the



CURVE 5.—YIELD OF JUICE PER 100 GRMS.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Volume + 5·0.
○ Gros Maroc.	Curve = Volume + 10·0.
△ Barbarossa.	Curve = Volume + 15·0.
* Waltham Cross.	Curve = Volume + 25·0.
● Flaming Tokai.	Curve = Volume + 35·0.

six varieties can be made. In the case of White Hanepoot and Red Hanepoot the maximum value was about 70 per cent., attained about 26th-27th February. Gros Maroc and Barbarossa reached a maximum of about 72-75 per cent. a few days earlier. In the case of Waltham Cross and Flaming Tokai the maximum yield of about 75 per cent. was reached about 25th February. After these dates the yield of juice began to diminish, and it may be supposed that further accumulation of water in the berry ceases. The berry has therefore reached its maximum "juice capacity," and further changes bring about a concentration of solids in the juice.

In considering these facts it is clear that so far as the physical changes are concerned, the maximum development has occurred about the beginning of March, and after this period the grapes could be considered ripe. The data in Table VII, based upon this conclusion, could be used to determine the physical aspect of a ripe grape.

TABLE VII.

Mature or Ripe Grapes.

	Average Weight in grms.	Average Volume in c.c.	Density of Berry.	Yield of Juice from 100 grms.
White Hanepoot	5·95	5·60	1·080	68·5
Red Hanepoot	5·95	5·65	1·065	69·0
Gros Maroc	4·95	4·60	1·070	72·0
Barbarossa	4·75	4·50	1·060	73·5
Waltham Cross	6·40	6·10	1·050	74·5
Flaming Tokai	6·45	6·20	1·060	74·0

These figures clearly show that the six varieties could be grouped into three sets of two each.

B.—CHEMICAL COMPOSITION OF THE JUICE.

Since all fruits, when subjected to pressure, yield a juice which contains the principal portion of their palatable constituents, a study of the composition of the juices is an important aspect of an investigation of the fruits. The results of the chemical examination of the juice expressed from each variety of grape are collected in Tables VIII-XIII.

As was to be expected, the density, degrees Balling, and glucose increase for all varieties during the whole period. The percentage of glucose followed closely the reading of the Balling hydrometer, the maximum value of the former being about 19 per cent. Table varieties of grapes do not generally have so high a content of sugar as those used for wine-making. The average sugar-content of 44 samples of wine grapes has been found to be 21.3 per cent., with a maximum of 30.5 per cent.* The acidity decreased during the period but there seemed to be a tendency for the amount of acid to reach a limiting value of .6-.7 per cent. The changes in sugar and acid are not inversely proportional to one another, but it is clear that a

* Frater: Dept. of Agr. Bull., Division of Chem. Series No. 32.

necessary condition of ripeness is a maximum sugar-content, together with a minimum acidity. The general tendency for the absorption of permanganate to increase is clear, but this change can hardly be correlated with the change in any one of the constituents of the berry since practically all organic substances will reduce potassium permanganate under similar conditions. The change simply indicated that the production of reducing substances proceeded during the process of ripening. The total soluble nitrogen decreased to a minimum and then seemed to increase slightly, while the ammoniacal nitrogen showed a continuous decrease during the whole period.

The results, expressed graphically, emphasize these facts and will be dealt with in more detail when discussing the curves.

Table VIII.
White Hanepoot.

Date.	Density of Juice, 20°/4°.	Balling at 20° C.	Grms. per 100 c.c. Juice. Glucose.	Acidity as grms. Tartaric Acid.	Total Soluble Nitrogen.	Ammonia Nitrogen.	Soluble Proteins.	$_pH$ of Juice.	C.c. of N/10 KM_nO_4 per 1 c.c. Juice.
28.1.25	1·0402	10·5	7·02	2·81	·0401	·0053	·218	—	—
4.2.25	1·0453	11·6	8·36	1·93	·0356	·0050	·191	2·71	123·5
11.2.25	1·0589	15·0	13·27	1·45	·0274	·0040	·146	2·91	120·5
18.2.25	1·0644	16·1	15·01	1·20	·0215	·0035	·113	3·05	125·5
25.2.25	1·0744	18·5	17·99	·76	·0225	·0027	·124	3·02	144·0
4.3.25	1·0771	19·1	18·48	·73	·0268	·0021	·154	3·53	151·0
11.3.25	1·0833	20·5	19·22	·68	·0374	·0015	·224	3·71	174·0

Table IX.
Red Hanepoot.

28.1.25	1·0371	9·8	7·69	3·10	·0310	·0049	·163	—	—
4.2.25	1·0502	12·9	10·60	1·91	·0292	·0047	·153	2·89	93·5
11.2.25	1·0578	14·8	13·38	1·45	·0213	·0038	·109	2·69	102·0
18.2.25	1·0673	16·9	15·63	1·13	·0154	·0031	·077	2·91	108·5
25.2.25	1·0684	17·0	16·60	·84	·0155	·0022	·083	3·13	147·5
4.3.25	1·0804	19·9	19·12	·70	·0212	·0016	·123	3·28	146·7
11.3.25	1·0794	19·7	18·83	·67	·0291	·0017	·171	3·59	148·0

Table X.
Gros Maroc.

28.1.25	1·0297	7·9	3·78	3·72	·0358	·0059	·187	—	—
4.2.25	1·0384	10·2	8·00	2·68	·0345	·0059	·179	2·98	116·0
11.2.25	1·0537	13·7	12·06	1·71	·0308	·0053	·159	3·15	115·5
18.2.25	1·0513	13·1	11·97	1·67	·0210	·0037	·108	3·21	132·5
25.2.25	1·0598	15·1	14·30	1·25	·0217	·0034	·114	3·23	137·0
4.3.25	1·0737	18·4	17·50	·91	·0288	·0028	·163	3·28	144·0
11.3.25	1·0762	18·9	17·45	·90	·0365	·0029	·210	3·27	165·3

Table XI.

Barbarossa.

Date.	Density of Juice, 20°/4°.	Balling at 20° C.	Grms. per 100 c.c. Juice.					$_pH$ of Juice.	C.c. of N/10 $KMnO_4$ per 1 c.c. Juice.
			Glucose.	Acidity as grms. Tartaric Acid.	Total Soluble Nitrogen.	Ammonia Nitrogen.	Soluble Proteins.		
28.1.25	1·0214	5·9	4·23	3·31	·0305	·0079	·141	—	103·5
4.2.25	1·0399	10·3	7·95	2·25	·0309	·0077	·145	2·63	105·0
11.2.25	1·0484	12·5	10·41	1·84	·0262	·0055	·129	2·86	105·0
18.2.25	1·0512	13·2	11·84	1·53	·0231	·0051	·113	3·18	116·0
25.2.25	1·0645	16·1	15·90	·81	·0215	·0034	·113	3·68	130·5
4.3.25	1·0677	16·9	16·24	·67	·0270	·0030	·150	3·69	135·5
11.3.25	1·0748	18·4	17·20	·67	·0343	·0018	·203	3·29	164·8

Table XII.

Waltham Cross.

28.1.25	1·0390	10·1	7·54	2·04	·0412	·0095	·198	—	97·5
4.2.25	1·0423	11·1	8·67	1·61	·0400	·0091	·193	2·35	95·3
11.2.25	1·0532	13·6	11·92	1·11	·0333	·0072	·163	2·62	110·0
18.2.25	1·0632	16·1	14·97	·83	·0247	·0048	·124	3·08	127·5
25.2.25	1·0799	19·7	18·99	·64	·0296	·0037	·152	3·69	132·0
4.3.25	1·0661	16·7	15·93	·70	·0309	·0032	·173	3·79	132·5
11.3.25	1·0678	16·9	15·87	·62	·0366	·0028	·211	3·46	146·8

Table XIII.

Flaming Tokai.

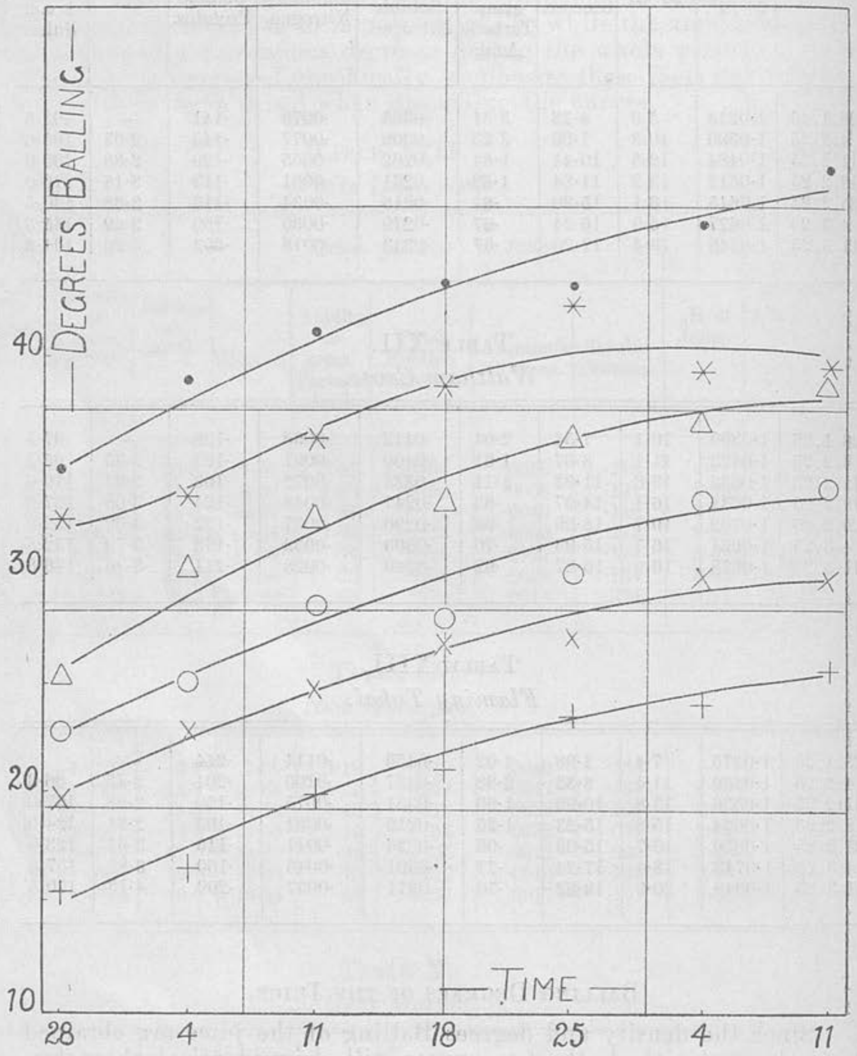
28.1.25	1·0275	7·4	2·98	4·02	·0456	·0114	·214	—	
4.2.25	1·0436	11·4	8·83	2·88	·0427	·0105	·201	2·45	96·3
11.2.25	1·0536	13·8	10·99	1·69	·0331	·0075	·160	2·68	107·0
18.2.25	1·0624	15·8	15·23	1·25	·0216	·0051	·103	2·94	124·0
25.2.25	1·0630	15·7	15·09	·96	·0225	·0041	·115	3·61	123·0
4.3.25	1·0743	18·4	17·24	·77	·0301	·0045	·160	3·88	157·8
11.3.25	1·0849	20·9	19·82	·70	·0371	·0037	·209	4·13	170·5

Balling Degrees of the Juice.

Since the density and degrees Balling of the juice are obtained by analogous methods the two curves will show identical characteristics. The curves showed a uniform increase in sugar-content, which gradually became less, indicating a cessation in the development of sugar. This method of estimating sugar is only accurate when applied to pure sugar solutions containing no other substances. It is therefore clear that the presence of other substances, strained through the linen filter, will so affect the density of the grape juice that this estimation of sugar can only be approximate. It would appear, however, that the production of fresh material in the berry practically ceased towards the end of the period.

Glucose in Juice.

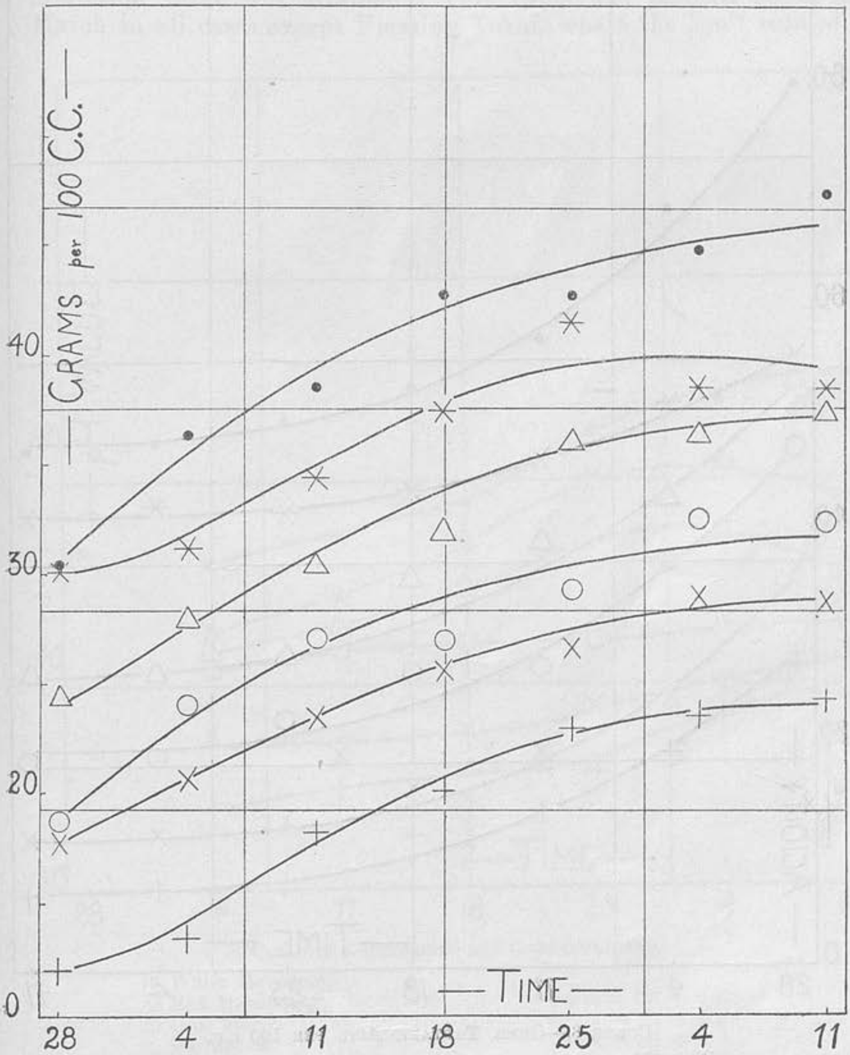
The curves show practically the same characteristics as those of Curve VI, except that the tendency to reach a maximum value at



Curve 6.—Degrees Balling of Juice.

+ White Hanepoot.	Curve = Balling + 5·0.
× Red Hanepoot.	Curve = Balling + 10·0.
○ Gros Maroc.	Curve = Balling + 15·0.
△ Barbarossa.	Curve = Balling + 20·0.
* Waltham Cross.	Curve = Balling + 22·5.
● Flaming Tokai.	Curve = Balling + 27·5.

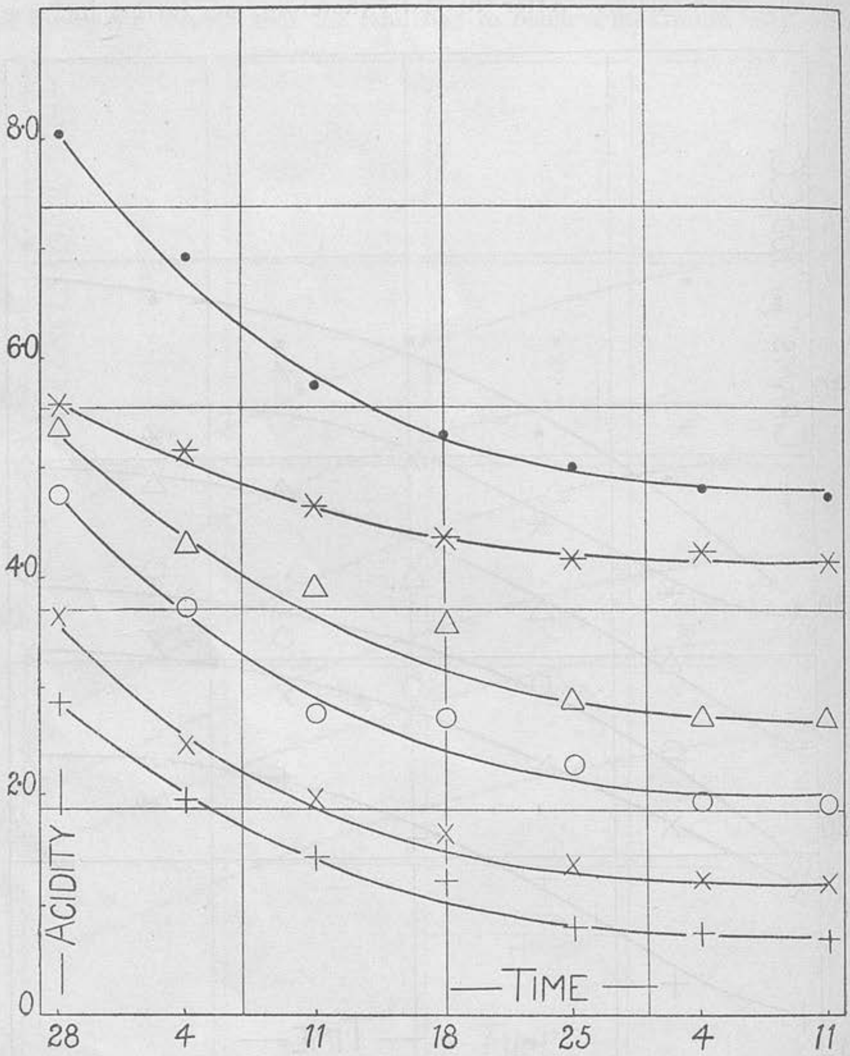
the end of the period is more obvious. In the initial stages the formation of sugar was rapid, but towards the end of the period the formation of sugar practically ceased. In all cases except Flaming Tokai the maximum amount had been attained practically about 4th March. At this date then the grapes could be considered ripe. In the case of Waltham Cross the period of maturity was apparently about a week earlier. After this date, therefore, any further increase



Curve 7.—Glucose in Juice.

+ White Hanepoot.
× Red Hanepoot. Curve = Glucose + 5·0.
○ Gros Maroc. Curve = Glucose + 10·0.
△ Barbarossa. Curve = Glucose + 15·0.
* Waltham Cross. Curve = Glucose + 17·5.
● Flaming Tokai. Curve = Glucose + 22·5.

in the sweetness of the grapes must be mainly due to a decrease in the amount of free acid in the grapes. Famintzin * has shown that during ripening the starch in the stems of grapes disappears, presumably in the formation of sugar in the berry. Under these circumstances it is justifiable to assume that when this store of starch has



CURVE 8.—GRMS. TARTARIC ACID PER 100 C.C.

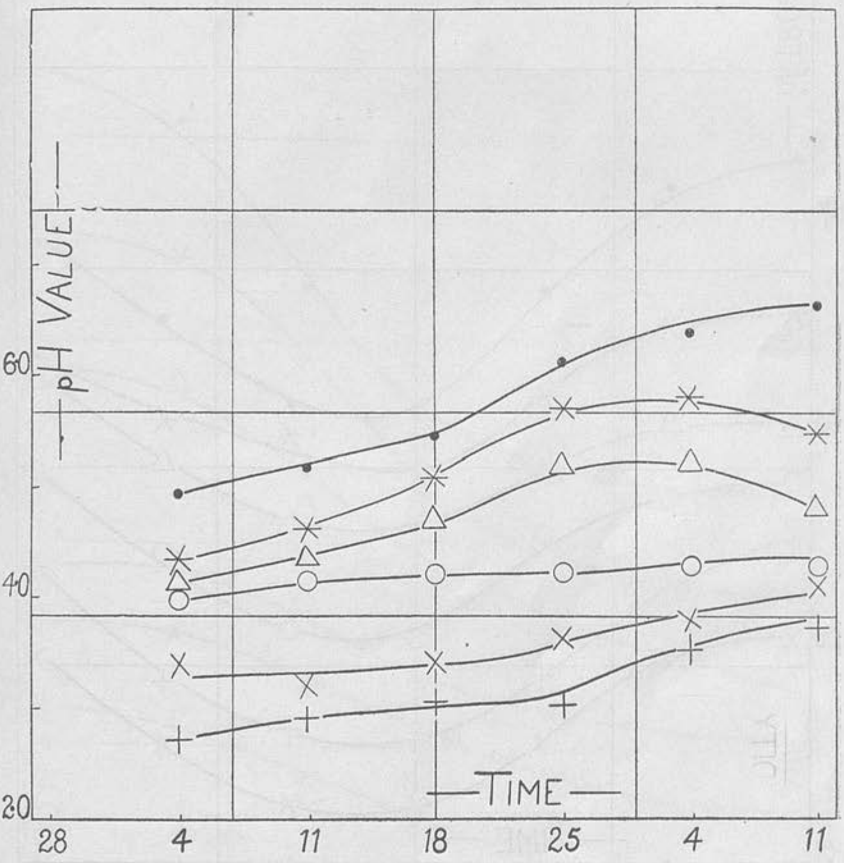
+ White Hanepoot.
× Red Hanepoot. Curve = Acid + 0·5.
○ Gros Maroc. Curve = Acid + 1·0.
△ Barbarossa. Curve = Acid + 2·0.
✱ Waltham Cross. Curve = Acid + 3·5.
● Flaming Tokai. Curve = Acid + 4·0.

* Famintzin *Ann. Oenal.*, 2, 242, 1871.

been utilized, the berry will gradually be cut off from the rest of the plant, and therefore further increase in sugar-content cannot be expected. Such a view agrees with the experimental data.

Acidity of Juice.

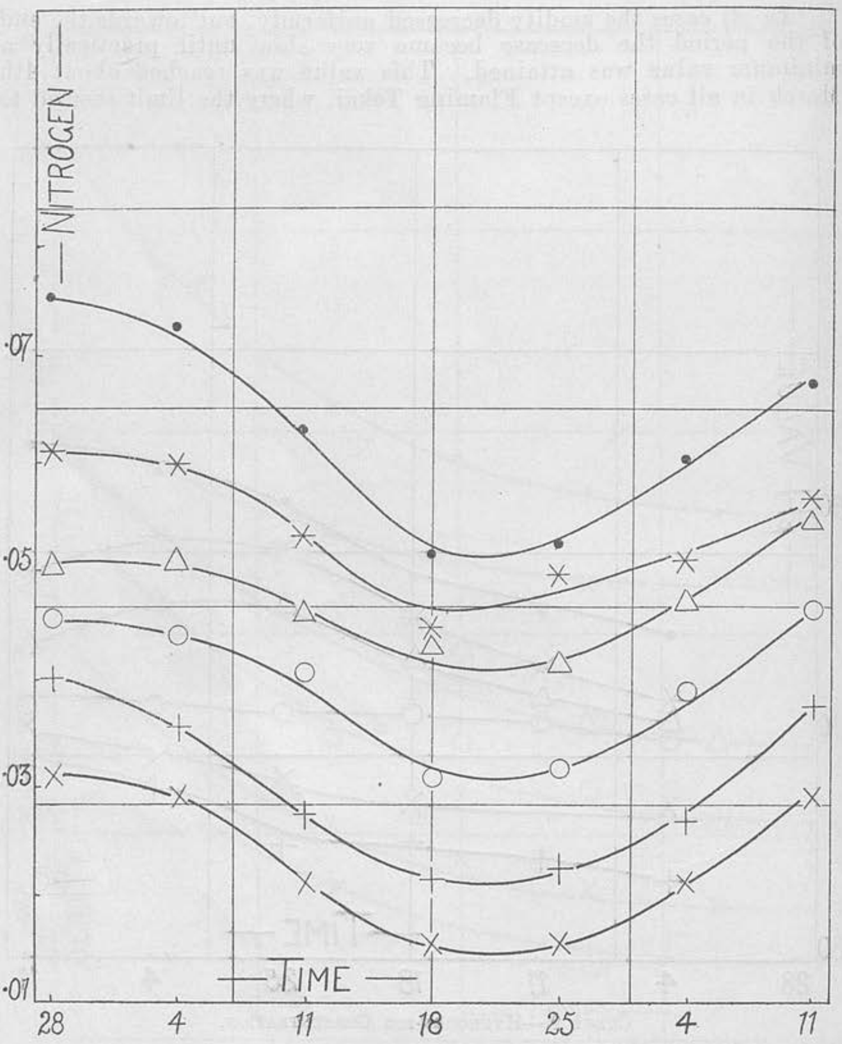
In all cases the acidity decreased uniformly, but towards the end of the period the decrease became very slow until practically a minimum value was attained. This value was reached about 4th March in all cases except Flaming Tokai, where the limit seemed to



Curve 9.—Hydrogen-ion Concentration.

+ White Hanepoot.	
× Red Hanepoot.	Curve = $_pH + 0{\cdot}5$.
○ Gros Maroc.	Curve = $_pH + 1{\cdot}0$.
△ Barbarossa.	Curve = $_pH + 1{\cdot}5$.
* Waltham Cross.	Curve = $_pH + 2{\cdot}0$.
• Flaming Tokai.	Curve = $_pH + 2{\cdot}5$.

be reached about a week later. In this latter case the initial decrease was much more rapid than in the other varieties. It would seem that the commencement of ripening of Flaming Tokai is retarded but that, once started, the ripening proceeds very rapidly. This characteristic is borne out by the previous curves. However, it would seem that by the first week in March the grapes are mature, although work * previously carried out indicates that there is still a slow decrease in acidity. Lewis† and Bioletti, Cruess, and Davi‡ have shown that



CURVE 10.—TOTAL SOLUBLE NITROGEN.

+ White Hanepoot.
× Red Hanepoot.
○ Gros Maroc. Curve = Nitro. + ·010.
△ Barbarossa. Curve = Nitro. + ·010.
* Waltham Cross. Curve = Nitro. + ·020·
● Flaming Tokai. Curve = Nitro. + ·030.

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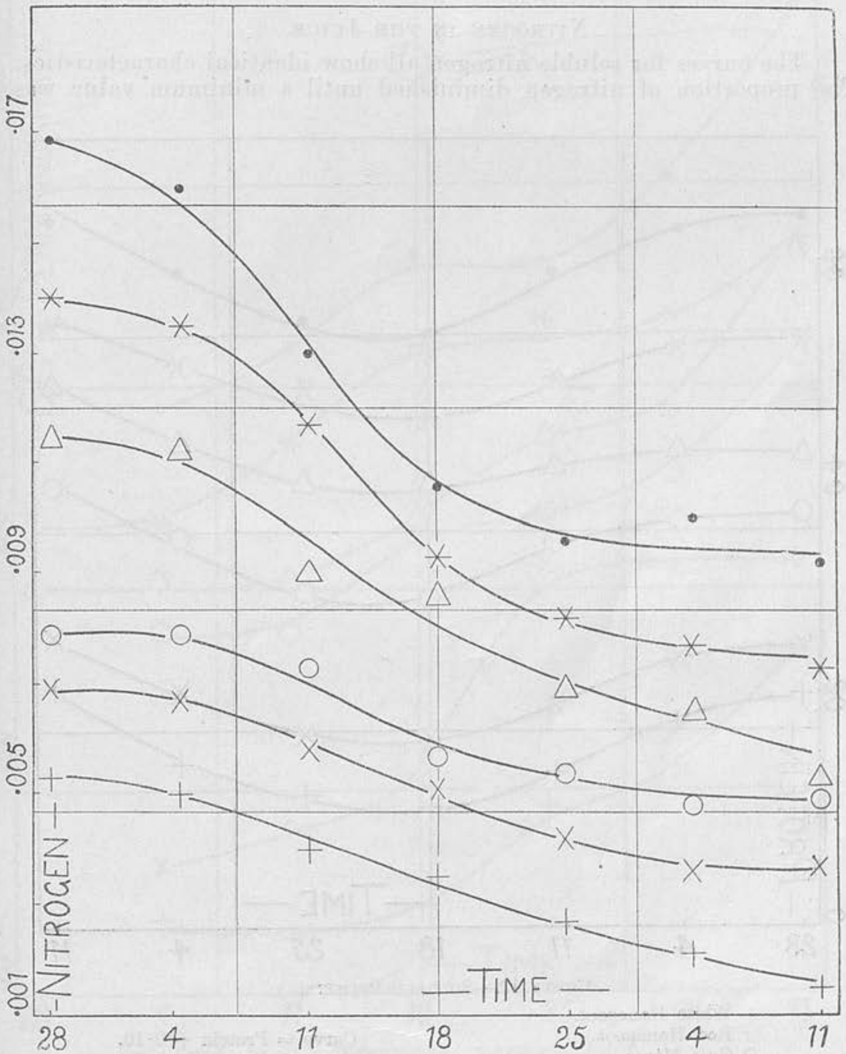
* Copeman : *Loc. cit.*
† Lewis : Bull. Dept. of Agr., 69, 1910.
‡ Bioletti, Cruess, and Davi : Univ. of Calif. Pubs. in Agr. Sc., Vol. III, No. 6, 1918.

the amount of cream of tartar increases slightly to a maximum and remains practically constant when the grapes are ripe. Therefore, the decrease in acidity must be due to the disappearance of the acid from the juice.

An increase in $_pH$ value indicates a decrease in free acidity and, as would therefore be expected, the curves all show an increase. The curves, obtained electrometrically, resemble very closely those



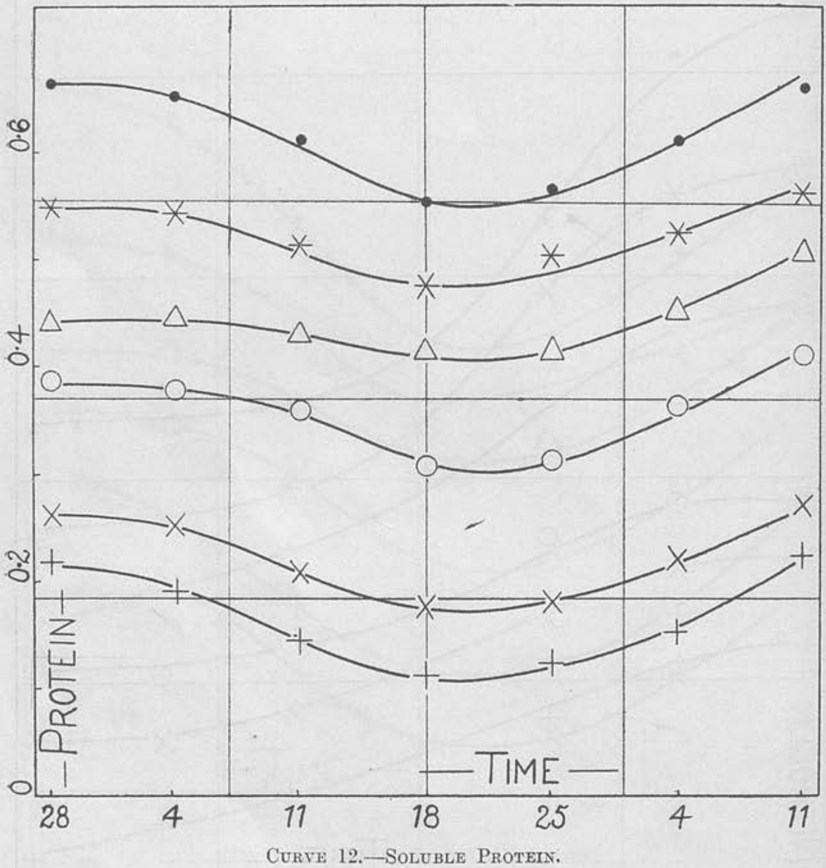
CURVE II.—AMMONIACAL NITROGEN.

+ White Hanepoot.	Curve = Nitro. + ·0020.
× Red Hanepoot.	Curve = Nitro. + ·0020.
○ Gros Maroc.	Curve = Nitro. + ·0035.
△ Barbarcssa.	Curve = Nitro. + ·0045.
✳ Waltham Cross.	Curve = Nitro. + ·0055.
● Flaming Tokai.	

obtained colorimetrically in 1923. The absolute values, however, are somewhat lower on account of the errors which are necessarily inherent in the colorimetric method. The change was greatest in the case of Flaming Tokai, probably due to the reason, mentioned above, of the retardation in ripening. In all cases, except Gros Maroc, there was a change in the rate of increase, and finally the values tended to reach a limiting value at a period which agrees with that found in the acidity curves.

Nitrogen in the Juice.

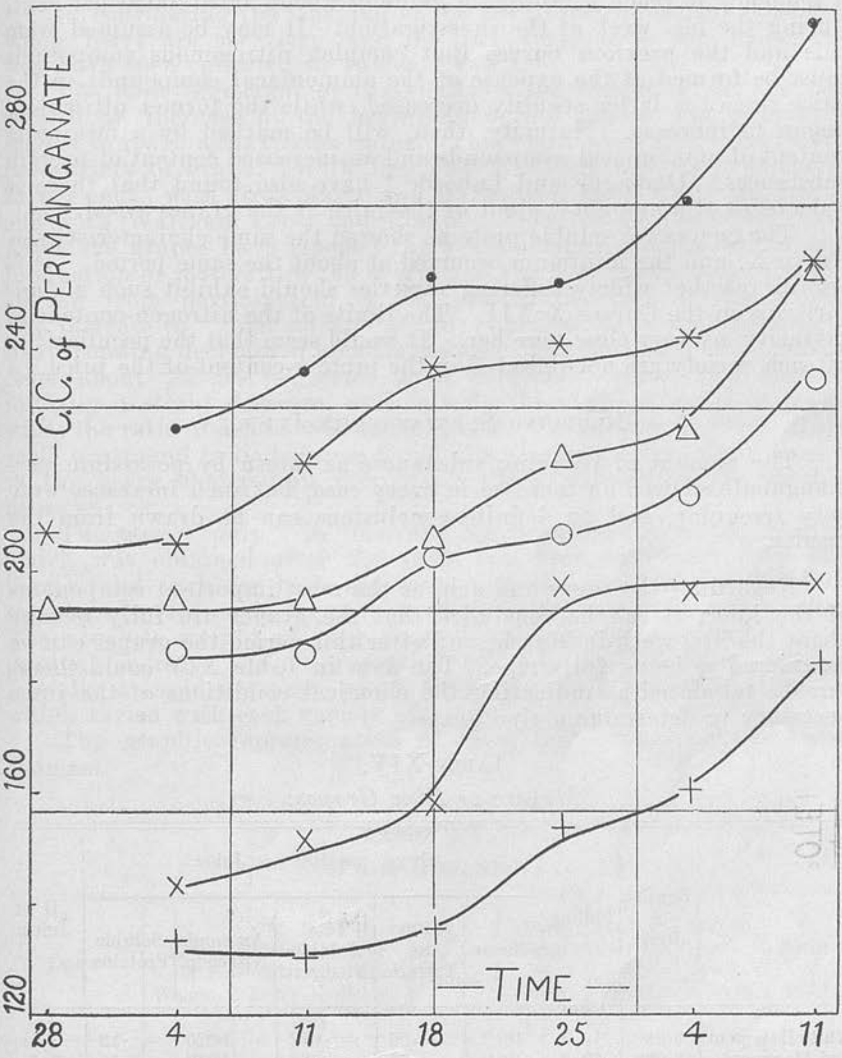
The curves for soluble nitrogen all show identical characteristics. The proportion of nitrogen diminished until a minimum value was



Curve 12.—Soluble Protein.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Protein + 0·10.
○ Gros Maroc.	Curve = Protein + 0·20.
△ Barbarossa.	Curve = Protein + 0·30.
* Waltham Cross.	Curve = Protein + 0·35.
• Flaming Tokai.	Curve = Protein + 0·45.

reached between 18th and 25th February, and after this there was a slight increase. During the initial period the grapes were ripening, the berry was swelling on account of a rapid influx of water, and sugar was being rapidly formed. These changes occurred at a greater rate than the changes in nitrogen-content, and therefore the latter showed a decrease. When these changes became retarded, the slight increase in nitrogenous bodies became apparent. There is a very slight increase in the absolute amount of nitrogen in the juice. Girard and Lindet * have drawn attention to the increase of nitrogen at maturity, and in



Curve 13.—C.c. Permanganate per c.c. Juice.

+ White Hanepoot.	Curve = c.c. + 10.
× Red Hanepoot.	Curve = c.c. + 50.
○ Gros Maroc.	Curve = c.c. + 70.
△ Barbarossa.	Curve = c.c. + 90.
✳ Waltham Cross.	Curve = c.c. + 110.
● Flaming Tokai.	Curve = c.c. + 130.

* Girard and Lindet: *Revue de Vit.*, 1898, p. 737.

all cases the absolute amount of nitrogen was found to be greater at maturity. The results of the present investigation are in agreement with these conclusions. The amount of nitrogen in the juice at maturity varied between fairly narrow limits, namely, about .030-.037 per cent.

After an initial period of about a week there was in all cases a continuous decrease of ammoniacal nitrogen, but there seemed to be a tendency to reach a minimum value of about .0020-.0030 per cent. during the last week of the investigation. It may be assumed from this and the previous curves that complex nitrogenous compounds must be formed at the expense of the ammoniacal compounds in the juice since the latter steadily decreased, while the former ultimately began to increase. Maturity, then, will be marked by a minimum content of ammoniacal compounds and an increased content of protein substances. Despagne and Laborde * have also found that there is a decrease of ammonia-content of the juice as the grapes ripen.

The curves for soluble proteins showed the same characteristics as Curve X, and the minimum occurred at about the same period. It is significant that widely differing varieties should exhibit such a similarity as in the Curves X-XII. The limits of the nitrogen-content at maturity lay very close together. It would seem that the peculiarities of each variety are not reflected in the protein-content of the juice.

Reducing Substances in Juice.

The amount of reducing substances as shown by potassium permanganate showed an increase in every case, but such increases were very irregular, and no definite conclusions can be drawn from the results.

Regarding the sugar and acid as the most important components of the juice, it can be concluded that the grapes are fully mature about the first week in March, and after this period the grapes can be considered as being fully ripe. The data in Table XIV could therefore be tabulated as indicating the chemical conditions of the juice necessary to determine a ripe grape.

Table XIV.

Mature or Ripe Grapes.

	Density of Juice.	Balling.	Grms. per 100 c.c. Juice.					pH of Juice.
			Glucose.	Acidity as Tartaric.	Total Soluble Nitrogen.	Ammonia Nitrogen.	Soluble Proteins.	
White Hanepoot	1·080	19·5	19·0	— ·65	+ ·032	— ·0020	+ ·19	3·6
Red Hanepoot.	1·080	19·8	19·0	— ·65	+ ·025	— ·0016	+ ·15	3·4
Gros Maroc....	1·075	18·6	17·4	— ·90	+ ·033	— ·0028	+ ·18	3·2
Barbarossa....	1·072	17·0	16·5	— ·67	+ ·031	— ·0020	+ ·18	3·6
Waltham Cross	1·067	16·8	16·0	— ·65	+ ·034	— ·0030	+ ·19	3·6
Flaming Tokai.	1·080	19·3	18·5	— ·70	+ ·003	— ·0035	+ ·18	4·0

— Not more than. + Not less than.

* Despagne and Laborde: *Revue de Vit.*, 1900, p. 189.

These figures agree very closely with the figures obtained in the same way in the 1923 investigation. Naturally, variations in sampling and conditions of growth would be expected to occur, but the limits will be very close to those given by the data in Table XIV.

C.—ANALYSIS OF THE BERRY.

In considering the ripening of the fruit, determinations upon the whole berry are necessary, and the data obtained in this investigation have been collected in Tables XV-XX.

The most important of these data is the "total solids," which showed an increase at the beginning of the period, but gradually tended to reach a maximum value. This value naturally varied with the variety of grape. With Red and White Hanepoots it is about 21 per cent., with Gros Maroc and Barbarossa about 18-19 per cent., and with Waltham Cross and Flaming Tokai about 19-20 per cent. After the grapes have ripened there would appear to be no further production of material in the berry, and the fruit would be gradually cut off from participation in the growth processes in the plant. The increase in "total solids" would, of course, be accompanied by a corresponding decrease of volatile matter. The ash in the berry varied from about .22-.56 per cent. as a maximum value, and showed initially a slight decrease, and latterly there was a rapid increase, while the ratio of ash to total solids showed similar peculiarities. This ratio was found to lie between 2 and 3 in all cases. The total nitrogen in the berry changed in very much the same way as the soluble nitrogen.

The term "pulp" in this case has been applied to the residue which was obtained after the juice had been expressed from the berries and includes both the skins and the seeds in the original sample. It represents the portion of the berry insoluble in the juice. The absolute weight of pulp showed a slight decrease and then a gradual increase. The proportion of pulp in the berry showed initially a rapid decrease, which tended to reach a minimum value, which varied with each variety of grape.

The graphic representation of these facts clearly shows these changes.

TABLE XV.

White Hanepoot.

Date.	% Loss of Weight.	% Total Solids in Berry.	% Ash in Berry.	Ratio : Ash/ Solids.	Total Nitrogen in Berry.	Insoluble Proteins in Berry.	Weight of Pulp in grms.	% Weigh of Pulp.
28.1.25.....	86·35	13·65	·302	2·21	·0688	·312	180·4	51·1
4.2.25.....	85·16	14·84	·271	1·82	·0712	·336	221·0	49·0
11.2.25.....	83·69	16·31	·268	1·64	·0701	·338	168·9	38·4
18.2.25.....	82·65	17·35	·373	2·15	·0650	·316	144·1	28·2
25.2.25.....	80·30	19·70	.421	2·14	·0630	·302	161·8	27·8
4.3.25.....	78·88	21·12	.481	2·28	·0648	·289	154·4	26·0
11.3.25.....	78·48	21·52	·465	2·16	·0730	·302	174·4	28·5

TABLE XVI.

Red Hanepoot.

Date.	% Loss of Weight.	% Total Solids in Berry.	% Ash in Berry.	Ratio: Ash/Solids.	Total Nitrogen in Berry.	Insoluble Proteins in Berry.	Weight of Pulp in grms.	% Weight of Pulp.
28.1.25.....	87·43	12·57	·269	2·14	·0585	·273	155·3	50·1
4.2.25.....	86·54	13·46	·229	1·70	·0614	·287	164·0	44·1
11.2.25.....	83·75	16·25	·310	1·91	·0633	·315	164·9	35·7
18.2.25.....	80·73	19·27	·378	1·97	·0607	·312	133·6	25·3
25.2.25.....	81·25	18·75	·442	2·36	·0555	·279	141·2	24·6
4.3.25.....	78·87	21·13	·444	2·10	·0659	·321	149·8	26·0
11.3.25.....	79·07	20·93	·357	1·71	·0711	·318	158·7	25·2

TABLE XVII.

Gros Maroc.

28.1.25.....	89·19	10·81	·333	3·08	·0690	·294	100·2	36·7
4.2.25.....	89·36	10·64	·231	2·17	·0681	·292	125·7	35·7
11.2.25.....	87·01	12·99	·332	2·56	·0676	·355	121·2	28·8
18.2.25.....	85·18	14·82	·377	2·54	·0661	·319	113·8	24·8
25.2.25.....	83·55	16·45	·479	2·91	·0662	·315	102·4	22·7
4.3.25.....	81·22	18·78	·444	2·64	·0693	·306	120·5	24·5
11.3.25.....	80·72	19·28	·386	2·00	·0740	·302	129·6	24·4

TABLE XVIII.

Barbarossa.

28.1.25.....	89·40	10·60	·277	2·62	·0835	·409	80·6	39·7
4.2.25.....	88·29	11·71	·229	1·95	·0819	·395	98·6	37·2
11.2.25.....	87·21	12·79	·311	2·43	·0662	·298	70·5	25·6
18.2.25.....	85·70	14·30	·352	2·46	·0615	·276	73·5	21·5
25.2.25.....	82·62	17·38	·492	2·83	·0592	·270	81·8	20·6
4.3.25.....	81·38	18·62	·461	2·47	·0581	·239	98·9	21·5
11.3.25.....	81·21	18·79	·383	2·04	·0632	·239	107·3	21·9

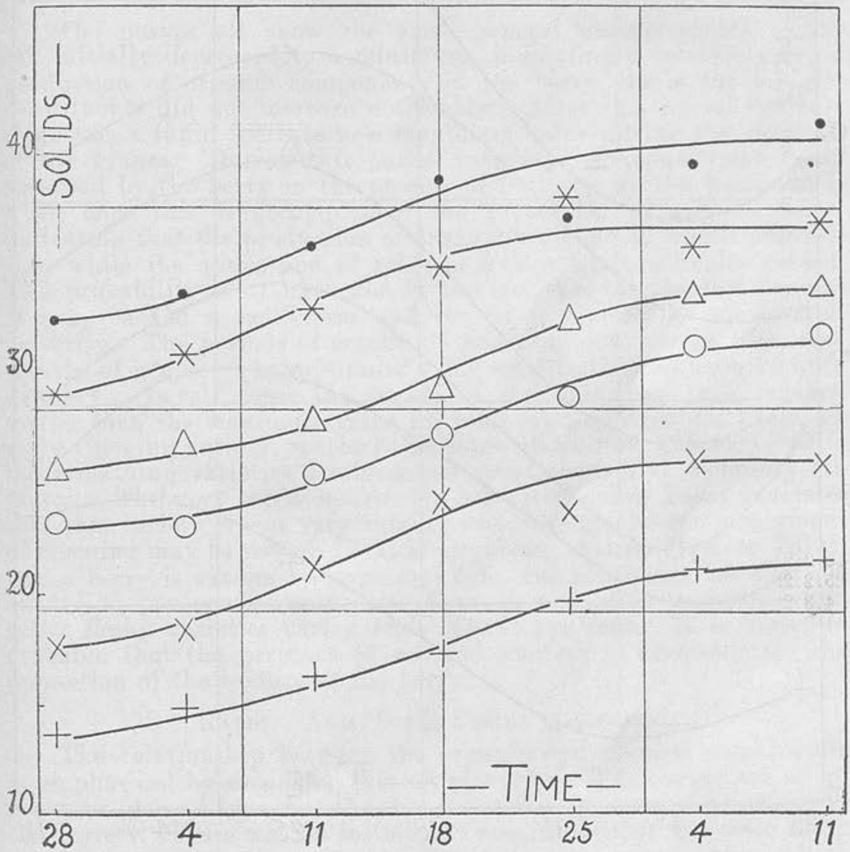
TABLE XIX.

Waltham Cross.

28.1.25.....	88·43	11·57	·251	2·17	·0520	·183	161·5	42·5
4.2.25.....	86·55	13·45	·245	1·82	·0558	·193	166·1	35·3
11.2.25.....	84·52	15·48	·380	2·47	·0575	·220	129·0	32·1
18.2.25.....	82·56	17·44	·443	2·54	·0549	·228	120·1	20·7
25.2.25.....	79·38	20·62	·482	2·37	·0543	·203	122·8	20·5
4.3.25.....	81·75	18·25	·425	2·30	·0511	·176	131·2	20·7
11.3.25.....	80·57	19·43	·400	2·06	·0604	·208	136·3	20·5

Table XX.
Flaming Tokai.

Date.	% Loss of Weight.	% Total Solids in Berry.	% Ash in Berry.	Ratio : Ash/ Solids.	Total Nitrogen in Berry.	Insoluble Proteins in Berry.	Weight of Pulp in grms.	% Weight of Pulp.
28.1.25.....	87·53	12·47	·288	2·31	·0594	·227	169·7	47·8
4.2.25.....	86·39	13·61	·236	1·74	·0592	·219	167·1	41·4
11.2.25.....	84·32	15·68	·250	1·61	·0564	·214	155·8	29·9
18.2.25.....	81·16	18·84	·458	2·43	·0540	·238	126·1	22·2
25.2.25.....	82·92	17·08	·509	2·99	·0510	·214	136·8	20·8
4.3.25.....	80·48	19·52	·558	2·86	·0529	·193	142·1	21·8
11.3.25.....	78·53	21·47	·498	2·32	·0605	·215	147·6	21·7

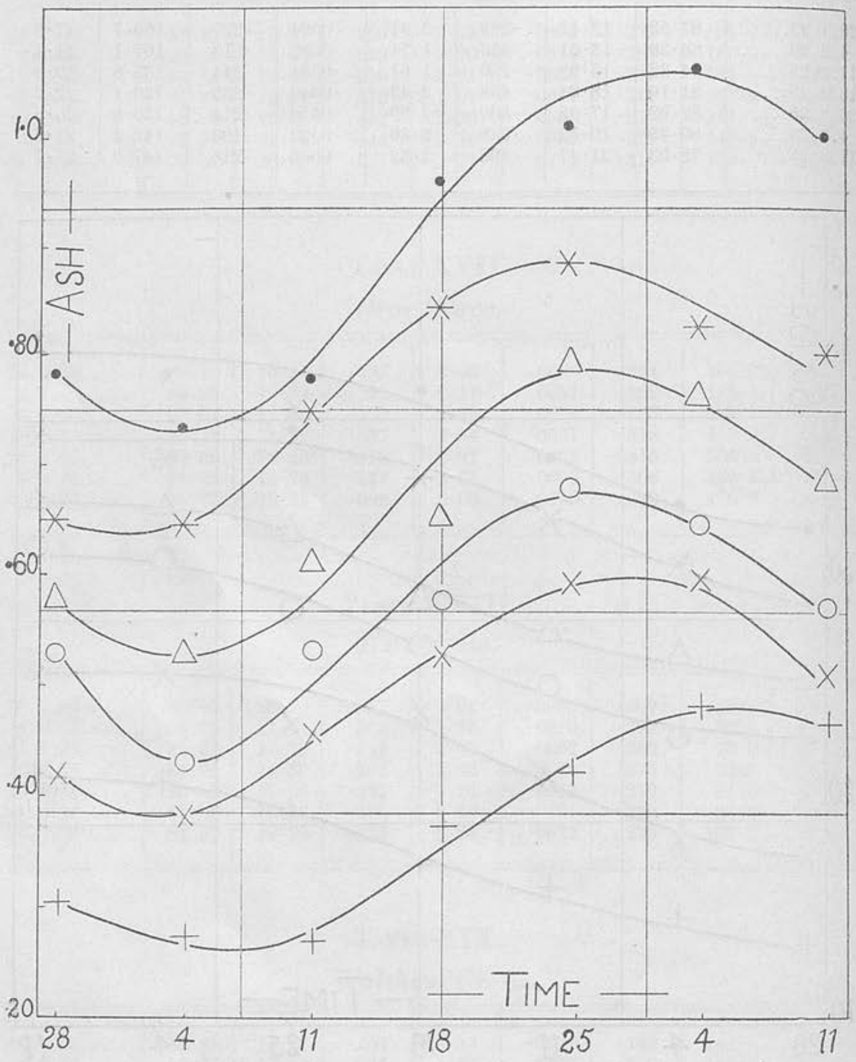


Curve 14.—Total Solids in Berry.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Solids + 5·0.
○ Gros Maroc.	Curve = Solids + 12·5.
△ Barbarossa.	Curve = Solids + 15·0.
* Waltham Cross.	Curve = Solids + 17·5.
• Flaming Tokai.	Curve = Solids + 20·0.

Total Solids in the Berry.

On account of the fact that the difference between the original weight of the berry and the "total solids" represents the loss of weight, the curve for the latter will be the complementary curve of the former. The latter curve, therefore, has been omitted. The curves for "total solids" all show the same characteristics. There was initially a slow increase, which became more rapid until about



Curve 15.—Ash in Berry.

+ White Hanepoot.
× Red Hanepoot. Curve = Ash + 0·15.
○ Gros Maroc. Curve = Ash + 0·20.
△ Barbarossa. Curve = Ash + 0·30.
* Waltham Cross. Curve = Ash + 0·40.
● Flaming Tokai. Curve = Ash + 0·50.

the beginning of March, where the increase practically ceased and a nearly constant value for the "total solids" was attained. The magnitude of this constant value varied slightly with each variety and has been already given (p. 25). With White Hanepoot, Waltham Cross, and Flaming Tokai the initial period of slow increase was not so clearly evident. With the exception of Flaming Tokai the final stage of apparently maximum total solids was clearly evident and occurred about 4th March (Waltham Cross was somewhat earlier). At this period then it may be concluded that the grapes are mature, and there is no further production of material in the berry. The lack of a clearly defined maximum in Flaming Tokai is further evidence of the more tardy development of that variety. Initially, the differences between "total solids" and sugars were large, but at maturity the difference was small and by increase in the former was mainly due to increase in sugar.

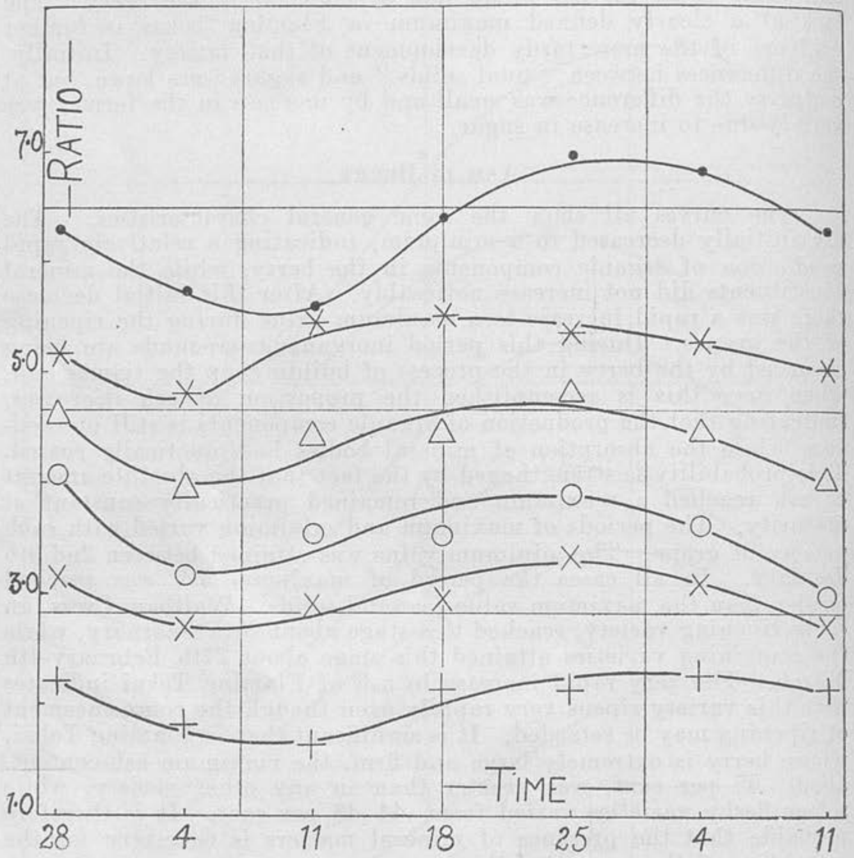
Ash in Berry.

The curves all show the same general characteristics. The ash initially decreased to a minimum, indicating a relatively rapid production of organic components in the berry, while the mineral constituents did not increase noticeably. After this initial decrease there was a rapid increase to a maximum value during the ripening of the grapes. During this period inorganic compounds are being absorbed by the berry in the process of building up the tissues and, when once this is accomplished the proportion of ash decreases, indicating that the production of organic components is still proceeding, while the absorption of mineral bodies has practically ceased. This probability is strengthened by the fact that the absolute amount of ash reached a maximum and remained practically constant at maturity. The periods of maximum and minimum varied with each variety of grape. The minimum value was attained between 2nd-9th January. In all cases the period of maximum ash was reached earlier than the maximum value for total solids. Waltham Cross, an early ripening variety, reached this stage about 25th February, while the remaining varieties attained this stage about 27th February-4th March. The very rapid increase in ash of Flaming Tokai indicates that this variety ripens very rapidly even though the commencement of ripening may be retarded. It is significant that in Flaming Tokai, whose berry is extremely large and firm. the maximum ash-content, about .55 per cent, was greater than in any other variety, while softer fleshy varieties varied from .44-.48 per cent. It is therefore probable that the presence of mineral matters is necessary for the promotion of the texture of the berry.

Ratio: Ash/Total Solids in Berry.

The relationship between the organic and mineral constituents is emphasized by means of this set of curves. The curves are all of the same general type, but the changes in the ratio varied according to the variety. There was an initial decrease, indicating the more rapid development of the organic components, to a minimum value, which was attained earliest in Waltham Cross and latest in Flaming Tokai in accordance with Curve XV. The minimum value varied with the variety of grape, between 1.5-2.2. After this stage the value of the ratio increased to a maximum indicating that the mineral constituents were being rapidly absorbed during this period. The maximum value for White Hanepoot, Red Hanepoot, and Waltham Cross is about 2.3-2.5, and for Gros Maroc, Barbarossa, and Flaming Tokai was about 2.8-2.9. There was subsequently a decrease in this ratio, so that, while the absorption of mineral matter had practically ceased, the production of organic matter was still proceeding.

Lewis* has shown that the cream of tartar increases fairly rapidly during ripening until a maximum is reached and then remains constant, and the quantities bear a simple relation to the potash



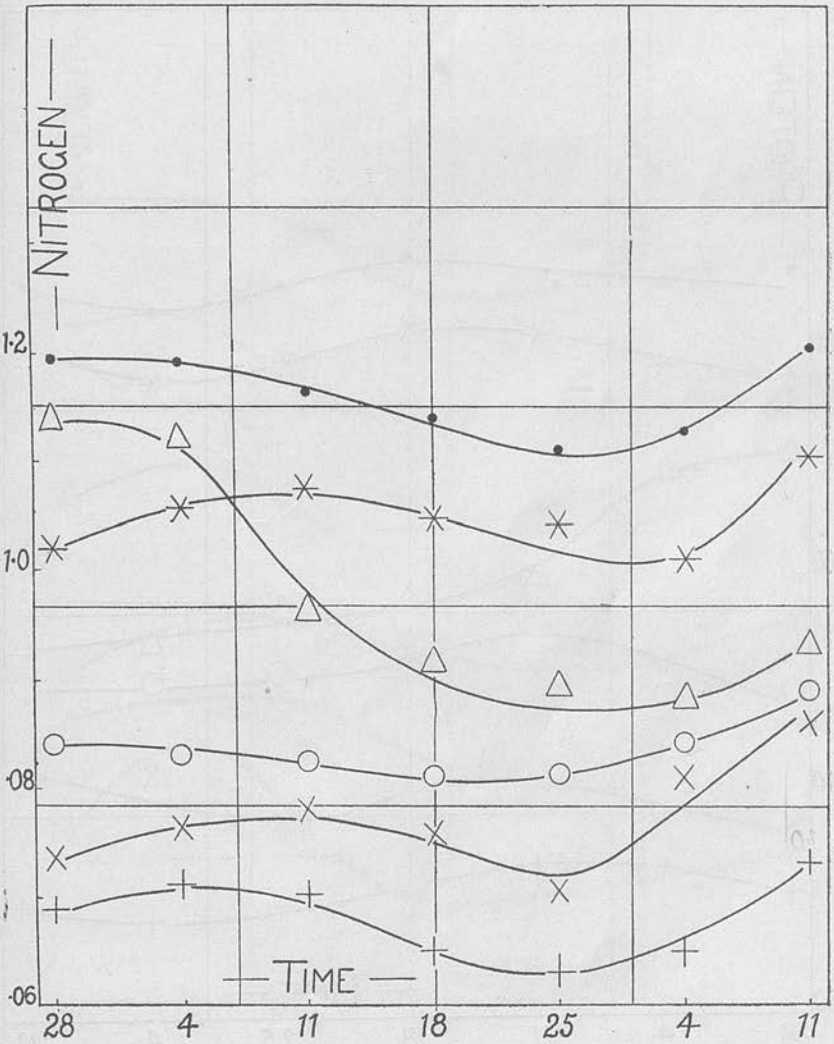
CURVE 16.—RATIO: ASH/TOTAL SOLIDS × 100.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Ratio + 1·0.
○ Gros Maroc.	Curve = Ratio + 1·0.
△ Barbarossa.	Curve = Ratio + 2·0.
* Waltham Cross.	Curve = Ratio + 3·0.
• Flaming Tokai.	Curve = Ratio + 4·0.

present, Therefore the increase in mineral-content is partly explained by the production of cream of tartar, and apparently this factor is connected with the decrease in acidity.

* Lewis: Bull. Dept. of Agr., 69, 1910.

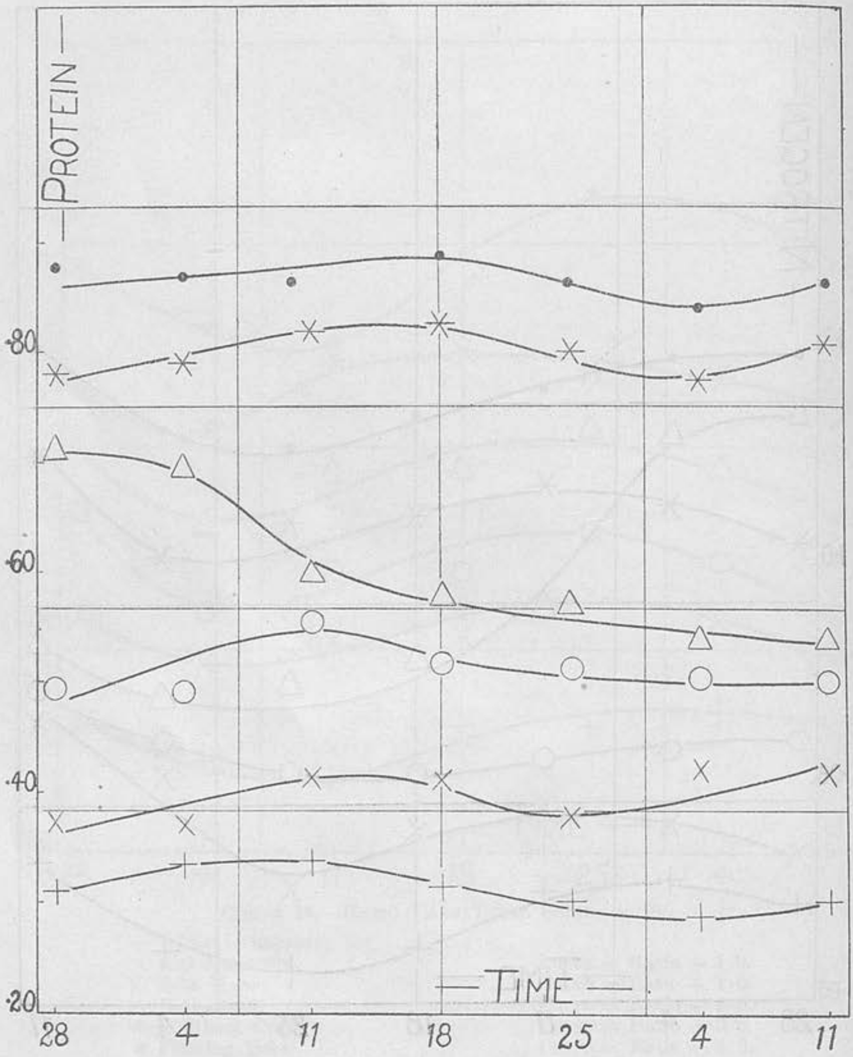
There was initially a slight increase to a maximum value, which, in the case of Gros Maroc, Waltham Cross, and Flaming Tokai, was either about 28th January or slightly earlier, in White Hanepoot about 4th February, and in Barbarossa and Red Hanepoot about a week later. After this stage the amount decreased to a minimum value, probably on account of the rapid accumulation of sugars and water in the berry, together with the consequent swelling. The amount



Curve 17.—Total Nitrogen in Berry.

+ White Hanepoot. Curve = Nitro. + ·015.
× Red Hanepoot. Curve = Nitro. + ·015.
○ Gros Maroc. Curve = Nitro. + ·030.
△ Barbarossa. Curve = Nitro. + ·050.
* Waltham Cross. Curve = Nitro. + ·060.
• Flaming Tokai.

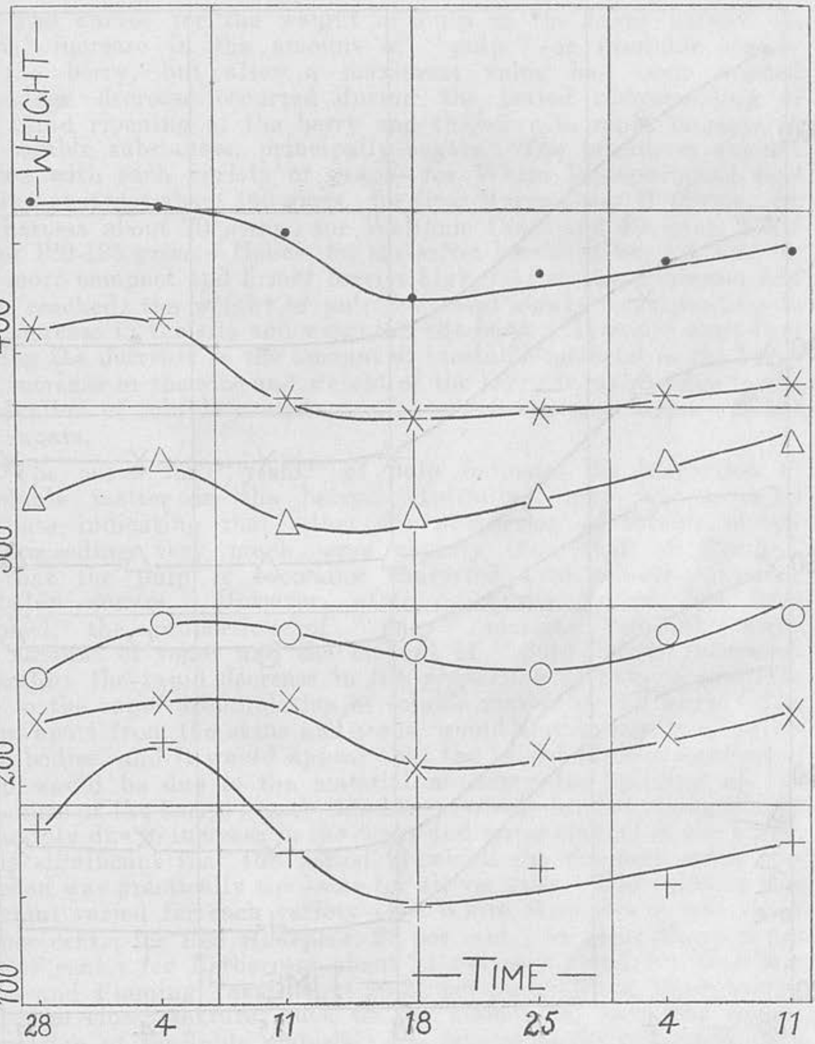
of nitrogen tended to increase slightly at maturity, so that the absolute amount is greatest in the mature berry. The period of minimum value varied slightly for each variety, but lies between 20th and 27th February. The minimum value does not vary much for each variety and lies between .50 and .65 per cent., and it would apear that the peculiarities of each variety are not greatly dependent upon the nitrogen-content of the berry.



CURVE 18.—INSOLUBLE PROTEINS IN BERRY.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Protein + 0·01.
○ Gros Maroc.	Curve = Protein + 0·20.
△ Barbarossa.	Curve = Protein + 0·30.
* Waltham Cross.	Curve = Protein + 0·60.
● Flaming Tokai.	Curve = Protein + 0·65.

The curves for insoluble protein follow fairly closely the curves for total nitrogen, except that there does not appear to be any very great change in protein-content. There was an initial increase to a maximum value, which was attained about 28th January for Barbarossa, about 7th February for White Hanepoot, about 11th February for Red Hanepoot

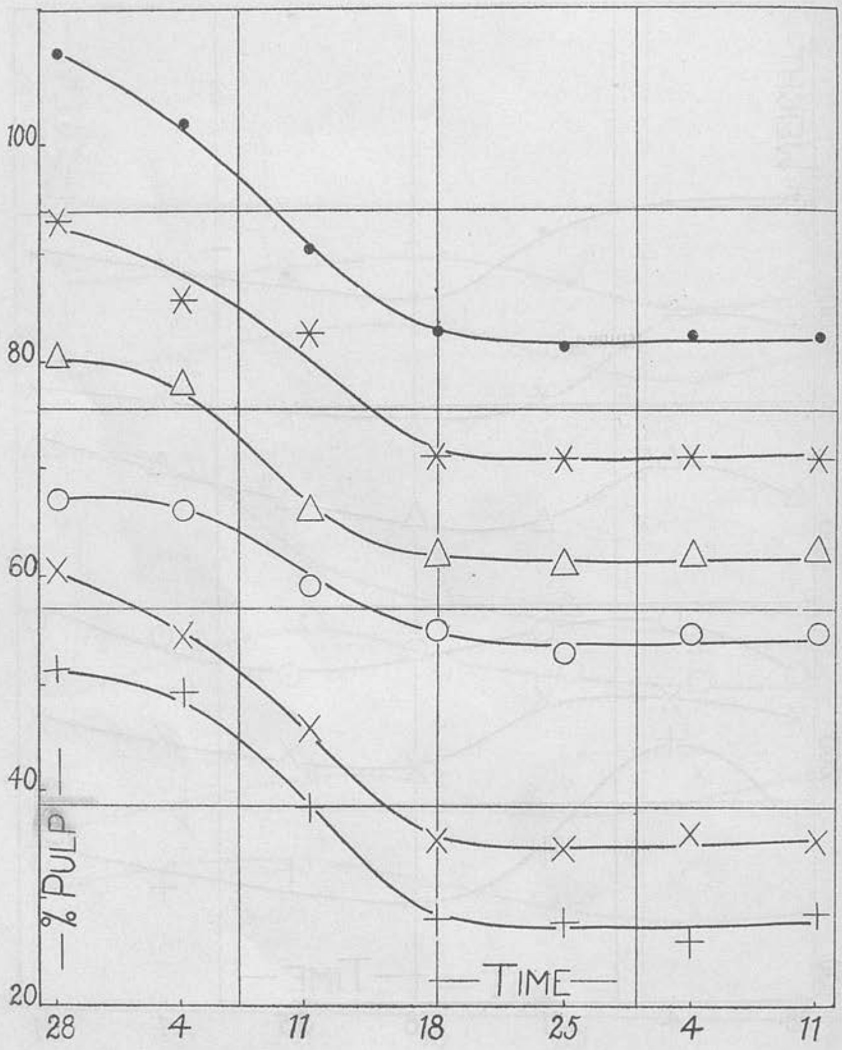


CURVE 19.—WEIGHT OF "PULP" IN BERRY.

+ White Hanepoot.
× Red Hanepoot.
○ Gros Maroc.
△ Barbarossa.
* Waltham Cross.
• Flaming Tokai.

Curve = Weight + 75.
Curve = Weight + 150.
Curve = Weight + 250.
Curve = Weight + 250.
Curve = Weight + 300.

and Gros Maroc, and about 18th February for Waltham Cross and Flaming Tokai. Subsequently there was a decrease in protein-content, indicating the more rapid production of other organic compounds. For White Hanepoot and Red Hanepoot the minimum value was about .28-.29 per cent., for Gros Maroc about .30 per cent.,



CURVE 20.—YIELD OF "PULP" PER 100 GRMS.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Yield + 10·0.
○ Gros Maroc.	Curve = Yield + 30·0.
△ Barbarossa.	Curve = Yield + 40·0.
* Waltham Cross.	Cruve = Yield + 50·0.
• Flaming Tokai.	Curve = Yield + 60·0.

for Barbarossa about .24 per cent., and for Waltham Cross and Flaming Tokai about .18-.19 per cent. It is significant that the large and firm berries showed the lowest value, and it would seem that the structure and texture of the berry is dependent upon the protein-content.

Pulp in the Berry.

The curves for the weight of pulp in the berry showed an initial increase in the amount of "pulp" or insoluble matter in the berry, but after a maximum value had been reached a sudden decrease occurred during the period corresponding to the rapid ripening of the berry and therefore to rapid increase in the soluble substances, principally sugars. The minimum amount varied with each variety of grape—for White Hanepoot and Red Hanepoot it was about 140 grms., for Gros Maroc about 100 grms., for Barbarossa about 70 grms., for Waltham Cross and Flaming Tokai about 120-125 grms. Hence, for the softer berries it was low and for the more compact and firmer berries high. After the minimum had been reached, the weight of pulp increased slowly corresponding to the increase in the size and weight of the berry. It would seem that during the decrease in the amount of insoluble material in the berry the increase in the size and weight of the berry is mainly due to the production of soluble constituents, of which the most important are the sugars.

The curve for "yield" of pulp indicates the proportion of insoluble matter in the berry. Initially, there was a rapid decrease indicating that either the production of soluble matter is proceeding very much more rapidly than that of "pulp," or that the pulp is becoming converted into soluble material, probably sugars. However, after a certain period has been reached, the proportion of "pulp" remains constant, while the amount of sugar and the amount of "pulp" both increased. Therefore the rapid decrease in the *proportion* of pulp is probably due to the rapid accumulation of soluble matter in the berry. The pulp, apart from the skins and seeds, would consist mostly of cellulosic bodies, and it would appear that the initial high proportion of pulp would be due to the material necessary for building up the structure of the berry. Once this has occurred, further changes must be mainly due to increase in the sugar and water content of the berry. It is significant that the period at which the constant value was reached was practically the same for all varieties. The value of this constant varied for each variety—for White Hanepoot it was about 27 per cent.; for Red Hanepoot, 25 per cent.; for Gros Maroc about 24 per cent.; for Barbarossa about 21 per cent.; and for Waltham Cross and Flaming Tokai about 20-21 per cent. Thus, those berries with the closer texture, such as the Hanepoots, have the higher proportion of insoluble material; the reverse is the case with such varieties as Flaming Tokai. (See remarks on "Ash in Berry," p. 29.)

Taking all the facts into consideration it may be concluded that the grapes are fully ripe by the first week in March, and further changes will not affect the factors which give the grape the characteristic of ripeness. The data in Table XXI would therefore be regarded as the limiting factors for a mature grape.

TABLE XXI.

	% Total Solids in Berry.	% Ash in Berry.	Ratio: Ash/Total Solids.	Total Nitrogen in Berry.	% Insoluble Proteins.	% Weight of Pulp.
White Hanepoot..	21·0	— ·48	— 2·2	+ ·064	+ ·29	27·0
Red Hanepoot....	21·0	— ·45	— 2·1	+ ·064	+ ·30	25·0
Gros Maroc.......	18·5	— ·44	— 2·6	+ ·070	+ ·30	24·0
Barbarossa........	18·5	— ·46	— 2·5	+ ·060	+ ·24	21·0
Waltham Cross...	19·0	— ·45	— 2·3	+ ·053	+ ·18	20·5
Flaming Tokai....	20·0	— ·50	— 2·8	+ ·053	+ ·19	21·0

— Not more than. + Not less than.

D.—ANALYSIS OF THE SEEDS.

On account of their oil-content, grape seeds have attracted increased attention of late years, but the use of seeds from table grapes for this purpose is obviously strictly limited. In the present work no attention has been given to the oil-content, and the proportion of pips, total solids, and ash in the pips have been determined. The results have been tabulated in Tables XXII-XXVII.

It is clear that the percentage of seeds decreased as the weight of berry increased. In general, the smaller berries had the higher percentage of seeds. Roughly the percentage of seeds at maturity varied between 1.0 and 2.5 per cent., the value for each variety varying very slightly during the latter week. The total solids showed a continuous increase during the whole period, together with a corresponding decrease of volatile matter. The amount of solids towards the end of the period was approximately 70 per cent. The ash in the seeds followed the same cycle of changes as the ash in the berry—there was an initial decrease, followed by an increase to a maximum value which varied between 1.5 and 1.7 per cent. of the seed. The ratio between the ash and total solids in the seeds showed a general tendency to decrease, and finally the value fell to about 2.0.

These changes will be more fully discussed when the graphical representation is considered, as the curves emphasize the changes more clearly.

TABLE XXII.

White Hanepoot.

Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio: Ash/Solids.
28.1.25....................	2·65	56·32	43·68	1·371	3·14
4.2.25....................	2·00	51·59	48·41	1·278	2·64
11.2.25....................	1·59	43·28	56·72	1·377	2·25
18.2.25....................	1·26	37·95	62·05	1·499	2·24
25.2.25....................	·96	36·08	63·92	1·562	2·44
4.3.25....................	1·06	35·29	64·71	1·510	2·33
11.3.25....................	1·32	25·31	74·69	1·405	1·88

TABLE XXIII.
Red Hanepoot.

Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio : Ash/Solids.
28.1.25	3·33	51·12	48·88	1·340	2·74
4.2.25	2·50	49·92	50·08	1·313	2·62
11.2.25	1·74	44·52	55·48	1·339	2·41
18.2.25	1·18	37·56	62·44	1·521	2·44
25.2.25	·93	37·87	62·13	1·568	2·52
4.3.25	1·04	33·25	66·75	1·763	2·44
11.3.25	1·14	26·13	73·87	1·731	2·34

TABLE XXIV.
Gros Maroc.

Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio : Ash/Solids.
28.1.25	3·64	54·50	45·50	1·467	3·22
4.2.25	2·73	52·59	47·41	1·331	2·80
11.2.05	2·12	48·11	51·89	1·566	3·02
18.2.25	1·83	43·98	56·02	1·701	3·04
25.2.25	1·80	44·40	55·60	1·667	3·00
4.3.25	1·78	42·24	57·76	1·585	2·75
11.3.25	1·87	31·40	68·60	1·518	2·21

TABLE XXV.
Barbarossa.

Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio : Ash/Solids.
28.1.25	4·16	53·13	46·87	1·282	2·74
4.2.25	2·88	46·41	53·59	1·249	2·33
11.2.25	2·23	43·65	56·35	1·517	2·69
18.2.25	1·72	41·29	58·71	1·576	2·68
25.2.25	1·44	40·69	59·31	1·586	2·67
4.3.25	1·49	38·38	61·62	1·472	2·39
11.3.25	1·61	28·56	71·44	1·338	1·87

TABLE XXVI.
Waltham Cross.

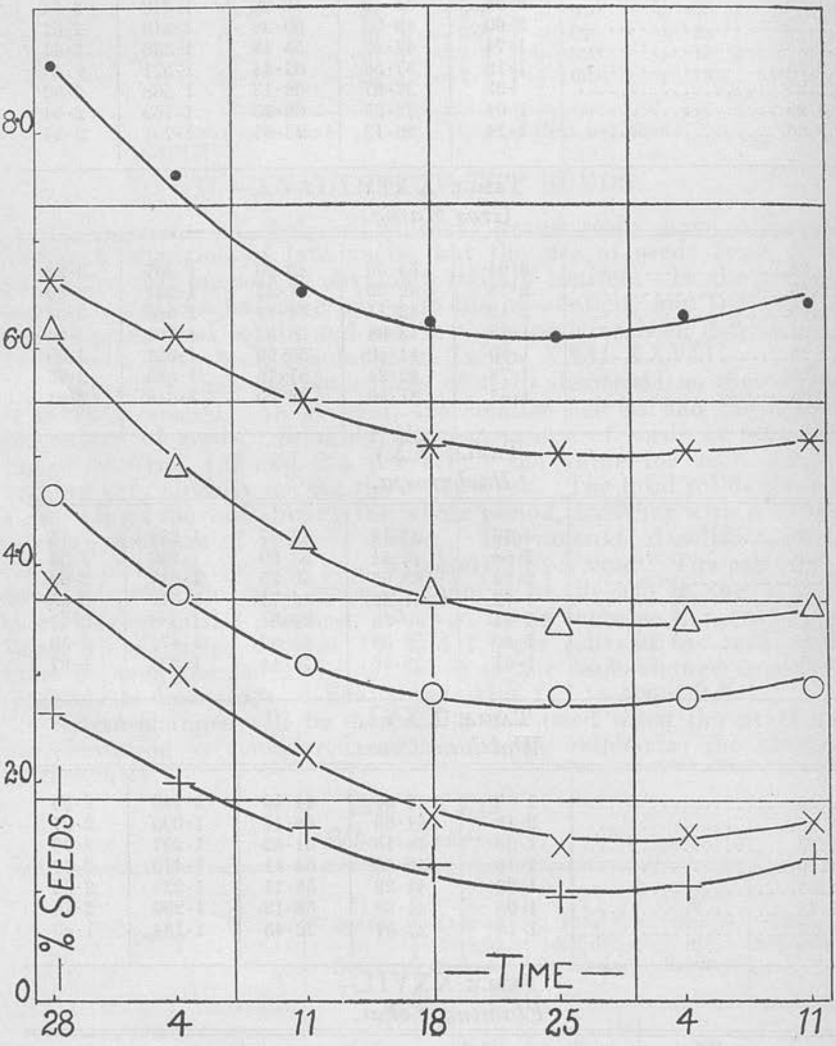
Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio : Ash/Solids.
28.1.25	2·66	55·90	44·10	1·149	2·60
4.2.25	2·13	51·86	48·14	1·095	2·27
11.2.25	1·68	48·18	51·82	1·297	2·28
18.2.25	1·10	45·59	54·41	1·410	2·59
25.2.25	1·03	44·29	55·71	1·328	2·38
4.3.25	1·05	41·88	58·12	1·256	2·16
11.3.25	1·15	27·57	72·43	1·184	1·63

TABLE XXVII.
Flaming Tokai.

Date.	% Seeds in Berry.	% Loss of Weight in Seeds.	% Total Solids in Seeds.	% Ash in Seeds.	Ratio : Ash/Solids.
28.1.25	4·63	59·97	40·03	1·458	3·64
4.2.25	3·60	56·66	43·34	1·334	3·08
11.2.25	2·52	50·21	49·79	1·362	2·73
18.2.25	2·24	48·08	51·92	1·532	2·95
25.2.25	2·10	48·07	51·93	1·516	2·92
4.3.25	2·30	43·81	56·19	1·453	2·59
11.3.25	2·42	36·27	63·73	1·322	2·07

Seeds in the Berry.

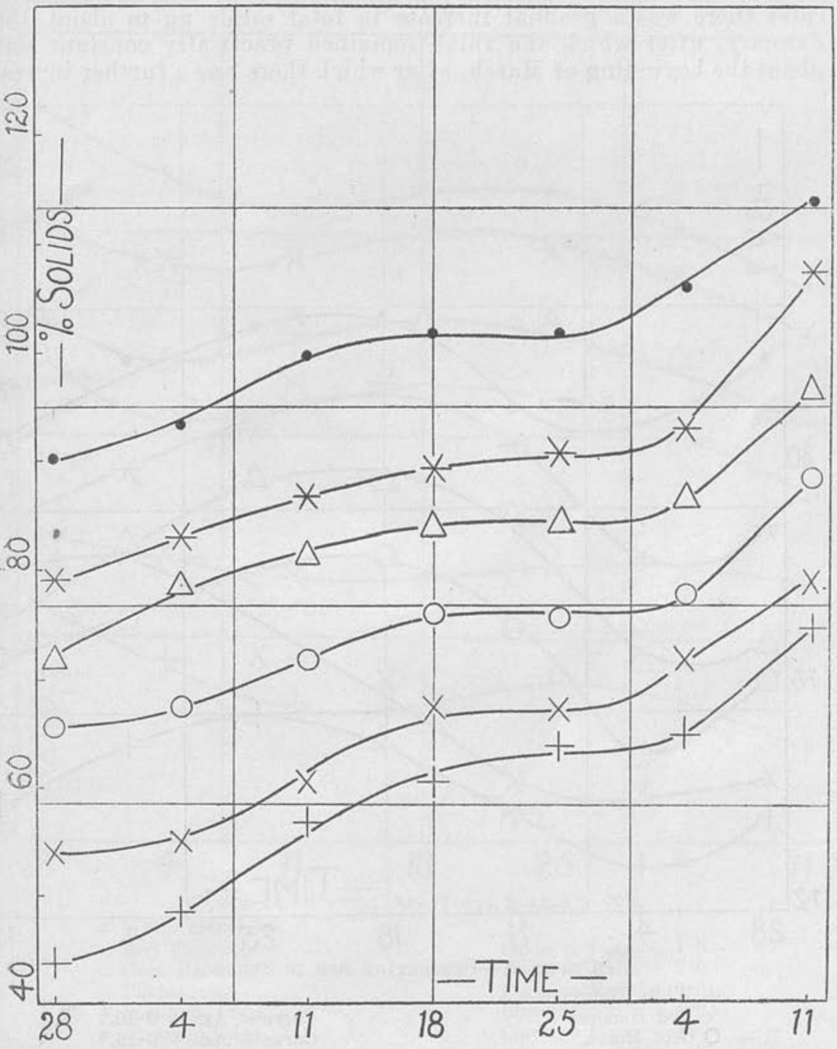
As the increase in the bunch lies mainly in the pulp of the berry it would be expected that the proportion of seeds would decrease and the curves plainly show this change. The proportion decreased to a minimum value and then remained practically constant or even showed a light increase. This minimum varied with each variety.



Curve 21.—Percentage Seeds in Berry.

+ White Hanepoot. Curve = % Seeds + 0·5.
× Red Hanepoot. Curve = % Seeds + 1·0.
○ Gros Maroc. Curve = % Seeds + 2·0.
△ Barbarossa. Curve = % Seeds + 4·0.
* Waltham Cross. Curve = % Seeds + 4·0.
● Flaming Tokai.

For White and Red Hanepoots it was about .95 per cent., for Waltham Cross about 1.0 per cent., for Barbarossa about 1.4 per cent., for Gros Maroc about 1.8 per cent., and for Flaming Tokai about 2.1 per cent. The closer-textured grapes showed a smaller percentage of seeds. In all cases the period of minimum value was about the last week in January.

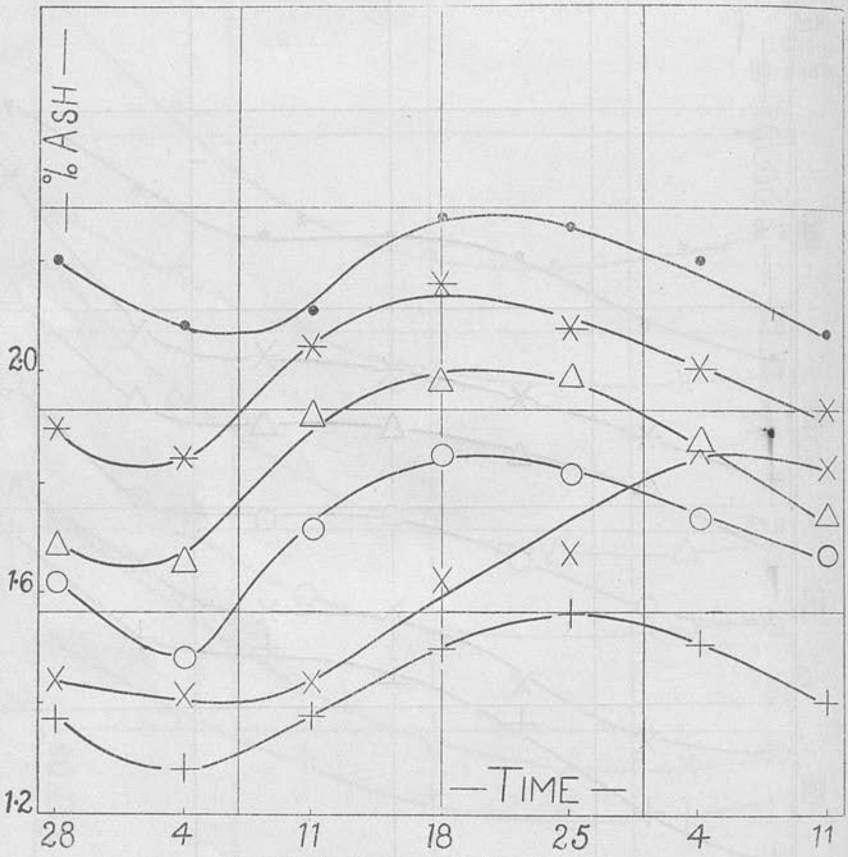


CURVE 22.—TOTAL SOLIDS IN SEEDS.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Solids + 5·0.
○ Gros Maroc.	Curve = Solids + 20·0.
△ Barbarossa.	Curve = Solids + 25·0.
∗ Waltham Cross.	Curve = Solids + 35·0.
● Flaming Tokai.	Curve = Solids + 50·0.

Total Solids in Seeds.

The difference between the original weight of seeds and the total solids represents loss of weight, and therefore the curve for the latter will form the complementary curve of the " total solid " curve. The curve of " loss of weight " has been, therefore, omitted. These curves all show practically identical characteristics, and therefore it is justifiable to conclude that the characteristics of any particular variety of grape are not reflected in the peculiarities of the seeds. In all cases there was a gradual increase in total solids up to about 18th January, after which the value remained practically constant until about the beginning of March, after which there was a further increase



Curve 23.—Percentage Ash in Seeds.

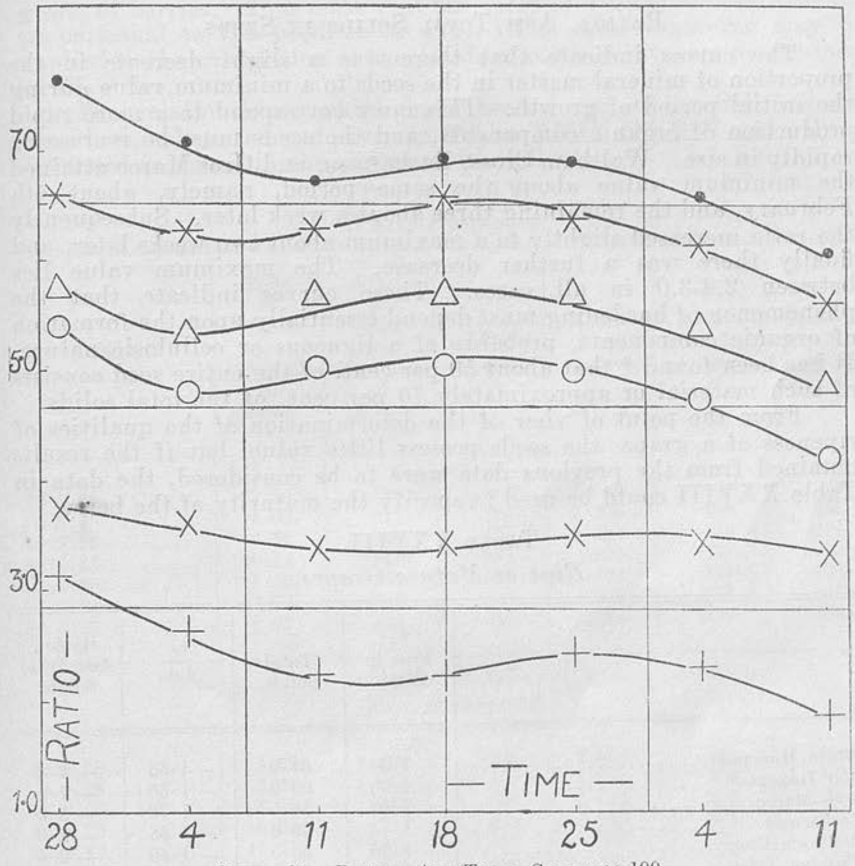
+ White Hanepoot.
× Red Hanepoot. Curve = Ash + 0·10.
○ Gros Maroc. Curve = Ash + 0·15.
△ Barbarossa. Curve = Ash + 0·40.
* Waltham Cross. Curve = Ash + 0·75.
● Flaming Tokai. Curve = Ash + 0·75.

in the total solids of the seeds. For Flaming Tokai the stationary value was about 52 per cent., for Waltham Cross and Gros Maroc about 55-56 per cent,. for Barbarossa about 59 per cent., and for

White and Red Hanepoots about 62-64 per cent. At maturity the seeds become hard, and it may be concluded that the increase in total solids about the beginning of March is closely related to this phenomenon. Therefore the grapes may be considered mature at this period and this conclusion agrees with the deductions drawn from the previous data.

ASH IN SEEDS.

The curves resemble closely the curves for percentage ash in the berry, as they showed similar maxima and minima. In all cases



CURVE 24.—RATIO: ASH/TOTAL SOLIDS × 100.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Ratio + 1·0.
○ Gros Maroc.	Curve = Ratio + 2·0.
△ Barbarossa.	Curve = Ratio + 3·0.
* Waltham Cross.	Curve = Ratio + 4·0.
• Flaming Tokai.	Curve = Ratio + 4·0.

the period of minimum ash was about 4th February, except Flaming Tokai, where it was slightly later. Prior to this the total solids are increasing, and therefore the development of the seed at this stage must depend upon the accumulation of organic constituents necessary for the growth of the seed. Subsequently the amount of ash increased to a maximum at a date and of a value which depended upon the variety of grape. This value was attained earliest by Waltham Cross, Barbarossa, and Gros Maroc about 18th February and latest by Red Hanepoot—about 4th March. The amount varied between 1.4 and 1.7 per cent. During this period of increase of the mineral-content, the seeds are rapidly absorbing inorganic salts. Subsequently the proportion of ash decreased, during which period the seeds have become set and are hardening. Since the total solids are still increasing, this process must be due largely to the formation of ligneous and cellulosic constituents.

Ratio: Ash/Total Solids in Seeds.

The curves indicate that there was a slight decrease in the proportion of mineral matter in the seeds to a minimum value during the initial period of growth. This must correspond to a more rapid production of organic components, and the seeds must be increasing rapidly in size. Waltham Cross, Barbarossa, and Gros Maroc attained the minimum value about the same period, namely, about 4th February, and the remaining three about a week later. Subsequently the ratio increased slightly to a maximum about two weeks later, and finally there was a further decrease. The maximum value lies between 2.4-3.0 in all cases. These curves indicate that the phenomenon of hardening must depend essentially upon the formation of organic components, probably of a ligneous or cellulosic nature. It has been found * that about 50 per cent. of the entire seed consists of such material or approximately 70 per cent. of the total solids.

From the point of view of the determination of the qualities of ripeness of a grape, the seeds possess little value, but if the results obtained from the previous data were to be considered, the data in Table XXVIII could be used to specify the maturity of the berry.

Table XXVIII.

Ripe or Mature Grapes.

	% Pips in Berry.	% Total Solids.	% Ash.	Ratio: Ash/Total Solids.
White Hanepoot	+ 1·00	64·0	— 1·55	— 2·4
Red Hanepoot	+ 1·00	62·0	— 1·55	— 2·5
Gros Maroc	+ 1·80	56·0	— 1·70	— 3·0
Barbarossa	+ 1·45	59·0	— 1·58	— 2·6
Waltham Cross	+ 1·00	55·0	— 1·40	— 2·4
Flaming Tokai	+ 2·10	52·0	— 1·53	— 2·9

+ Not less than. — Not more than.

E.—SOME QUANTITATIVE RELATIONSHIPS.

In considering the whole series of curves it is evident that the maximum amount of change in the grapes must have occurred prior to the 4th March and that subsequently the changes were relatively slight. It is clear that, when the grapes have fully matured, some equilibrium must be set up between the various factors which influence the condition of the grape and that this state will not be subject to

* Frater: *Loc. cit.*

much further change. An endeavour has been made to obtain some numerical relationship which would express this fact. The characteristics which are most important in determining the quality of the grape are the sugar and acidity. Therefore it would be expected that these factors would most likely exhibit such relationships, and indeed they have been found to show the most interesting results.

In the first place it must be pointed out that the yield of glucose from a given weight of berries may be obtained from the two factors—(*a*) weight of glucose in 100 c.c. juice, (*b*) amount of juice from 100 grms. of berries. It is clear that the yield of glucose will be directly proportional to the product $(a) \times (b)$. The same reasoning may be applied to the calculation of the yields of other substances determined in the juice.

The relationships, which have been found of special interest, have been calculated and given in Tables XXIX-XXXIV and will be discussed in detail in the curves which follow.

TABLE XXIX.
White Hanepoot.

Date.	Yield of Glucose per 100 grms. of Berry.	Yield of Acid per 100 grms. of Berry.	Ratio : Glucose/Solids.	Ratio : Acid/Glucose.	Ratio : Total N_2/Solids.	Ratio : Sol. N_2/Total N_2.
28.1.25..........	3.30	1·320	·242	4·003	·504	·274
4.2.25..........	4·08	·942	·275	2·308	·480	·244
11.2.25..........	7·72	·844	·474	1·092	·430	·228
18.2.25..........	10·14	·810	·584	·800	·375	·223
25.2.25..........	11·75	·496	·596	·423	·320	·233
4.3.25..........	12·74	·503	·603	·395	·307	·285
11.3.25..........	12·67	·448	·589	·354	·339	·338

TABLE XXX.
Red Hanepoot.

Date.	Yield of Glucose per 100 grms. of Berry.	Yield of Acid per 100 grms. of Berry.	Ratio : Glucose/Solids.	Ratio : Acid/Glucose.	Ratio : Total N_2/Solids.	Ratio : Sol. N_2/Total N_2.
28.1.25..........	3·69	1·488	·294	4·031	·465	·254
4.2.25..........	5·64	1·016	·419	1·801	·456	·253
11.2.25..........	8·13	·882	·500	1·084	·390	·204
18.2.25..........	10·94	·791	·568	·723	·315	·178
25.2.25..........	11·71	·593	·625	·506	·296	·197
4.3.25..........	13·10	·479	·620	·366	·312	·220
11.3.25..........	13·05	·464	·624	·356	·340	·284

TABLE XXXI.
Gros Maroc.

Date.	Yield of Glucose per 100 grms. of Berry.	Yield of Acid per 100 grms. of Berry.	Ratio : Glucose/Solids.	Ratio : Acid/Glucose.	Ratio : Total N_2/Solids.	Ratio : Sol. N_2/Total N_2.
28.1.25..........	2·33	2·288	·225	9·835	·639	·319
4.2.25..........	4·95	1·659	·465	3·350	·640	·314
11.2.25..........	8·15	1·155	·627	1·488	·520	·308
18.2.25..........	8·57	1·196	·578	1·395	·446	·228
25.2.25..........	10·42	·910	·634	·874	·402	·239
4.3.25..........	12·30	·640	·655	·520	·369	·292
11.3.25..........	12·27	·633	·636	·516	·384	·346

TABLE XXXII.

Barbarossa.

Date.	Yield of Glucose per 100 grms. of Berry.	Yield of Acid per 100 grms. of Berry.	Ratio : Glucose/ Solids.	Ratio : Acid/ Glucose.	Ratio Total N_2/ Solids.	Ratio : Sol. N_2/ Total N_2.
28.1.25..........	2·50	1·956	·236	7·823	·787	·216
4.2.25..........	4·80	1·359	·410	2·832	·699	·228
11.2.25..........	7·38	1·304	·577	1·767	·518	·281
18.2.25..........	8·86	1·145	·629	1·292	·430	·281
25.2.25..........	11·92	·607	·680	·509	·340	·272
4.3.25..........	11·92	·492	·675	·413	·312	·341
11.3.25..........	12·52	·488	·666	·390	·336	·395

TABLE XXXIII.

Waltham Cross.

28.1.25..........	4·17	1·127	·360	2·704	·449	·438
4.2.25..........	5·39	1·001	·401	1·858	·415	·446
11.2.25..........	7·71	·718	·498	·931	·372	·375
18.2.25..........	11·20	·621	·642	·554	·315	·337
25.2.25..........	13·98	·471	·678	·337	·286	·401
4.3.25..........	11·80	·519	·647	·439	·280	·448
11.3.25..........	11·80	·461	·637	·391	·311	·436

TABLE XXXIV.

Flaming Tokai.

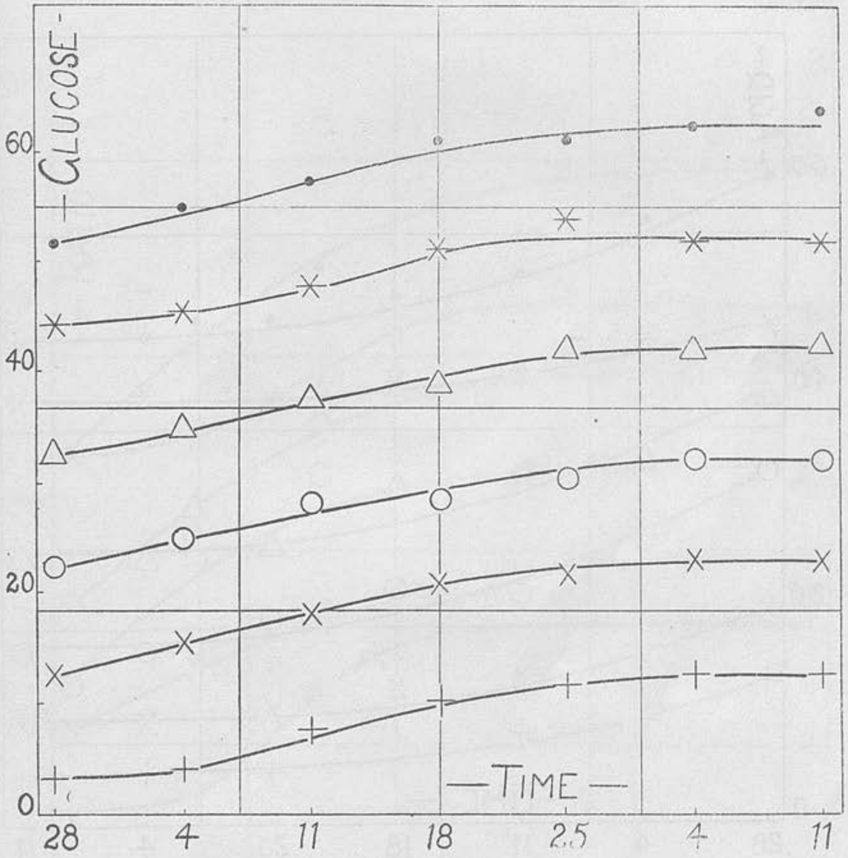
28.1.25..........	1·51	2·038	·121	13·48	·476	·389
4.2.25..........	4·98	1·625	·366	3·261	·435	·407
11.2.25..........	7·34	1·129	·468	1·538	·360	·392
18.2.25..........	11·18	·918	·593	·821	·287	·294
25.2.25..........	11·27	·717	·660	·636	·299	·330
4.3.25..........	12·60	·563	·646	·445	·271	·416
11.3.25..........	13·93	·492	·649	·353	·282	·431

YIELD OF GLUCOSE.

The curves indicate the amount of sugar which could be obtained from a given weight of berries. They all showed the same characteristics. There was a slow increase, which gradually reached a maximum value about the first week in March and then remained practically constant. Waltham Cross, an early ripening variety, seemed to reach the maximum somewhat earlier than the remaining varieties. A stage was therefore reached when the absolute amount of sugar remained practically constant. This must be regarded as an indication of the attainment of maturity by the berry, and therefore by the 4th March the grapes have become mature. The value of the maximum yield depended upon the variety of grape and was greatest in the case of the two Hanepoot varieties, at least in the case of Gros Maroc and Barbarossa. The taste alone would be sufficient to group these varieties in this way. From these curves it may be concluded that at maturity the data in Table XXXV could be used to determine the period at which the berry may be considered ripe.

Yield of Acid.

As was to be expected, the curves show that there was a decrease in the amount of acidity from a given weight of berries. The curves are all of a similar nature. Initially, the acidity decreased until,

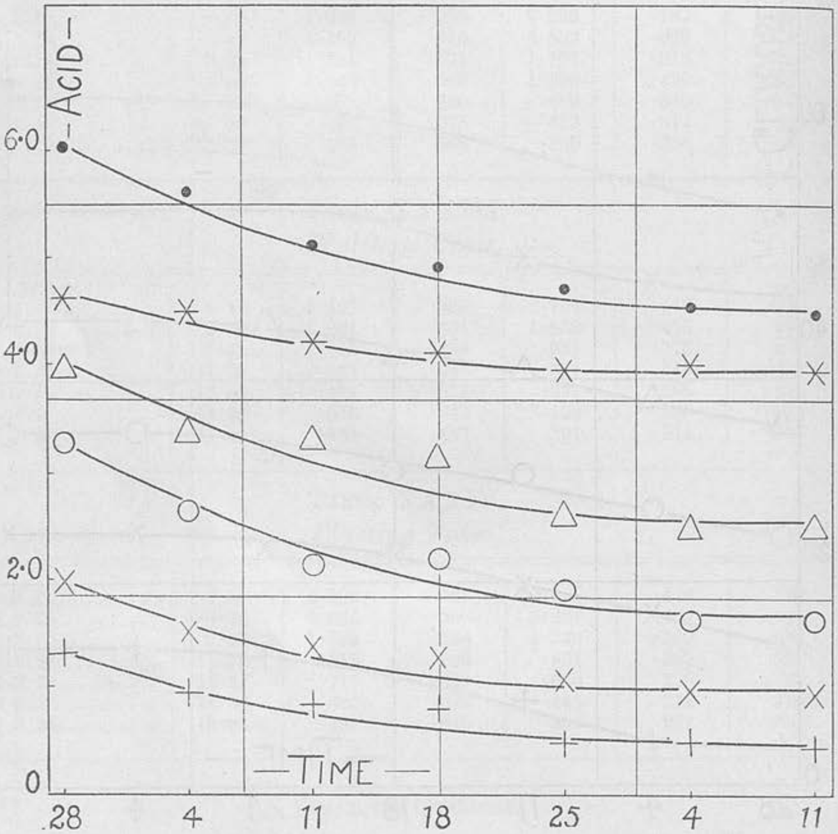


Curve 25.—Yield of Glucose per 100 grms.

+ White Hanepoot.
× Red Hanepoot. Curve = Yield + 10·0.
○ Gros Maroc. Curve = Yield + 20·0.
△ Barbarossa. Curve = Yield + 30·0.
* Waltham Cross. Curve = Yield + 40·0.
● Flaming Tokai. Curve = Yield + 50·0.

towards the end of the period, a practically constant minimum value was reached. The curve for Waltham Cross showed the least amount of decrease in free acid, probably due to the fact that this variety ripens early. After the first week in March there was practically no further change in the amount of acid and the grapes must be considered mature. Therefore it may be concluded that the data in Table XXXV may be regarded as the maximum yield of acid in the grapes at maturity.

The lowest yield was given by Waltham Cross, and both the Hanepoots gave similar yields only slightly greater than Waltham Cross. This result is in accordance with the taste of the grapes which is sweet with very little acidity. Barbarossa and Flaming Tokai gave the next highest yield, while Gros Maroc yielded the highest figure. These last three varieties are all grapes with a distinctly tart flavour.

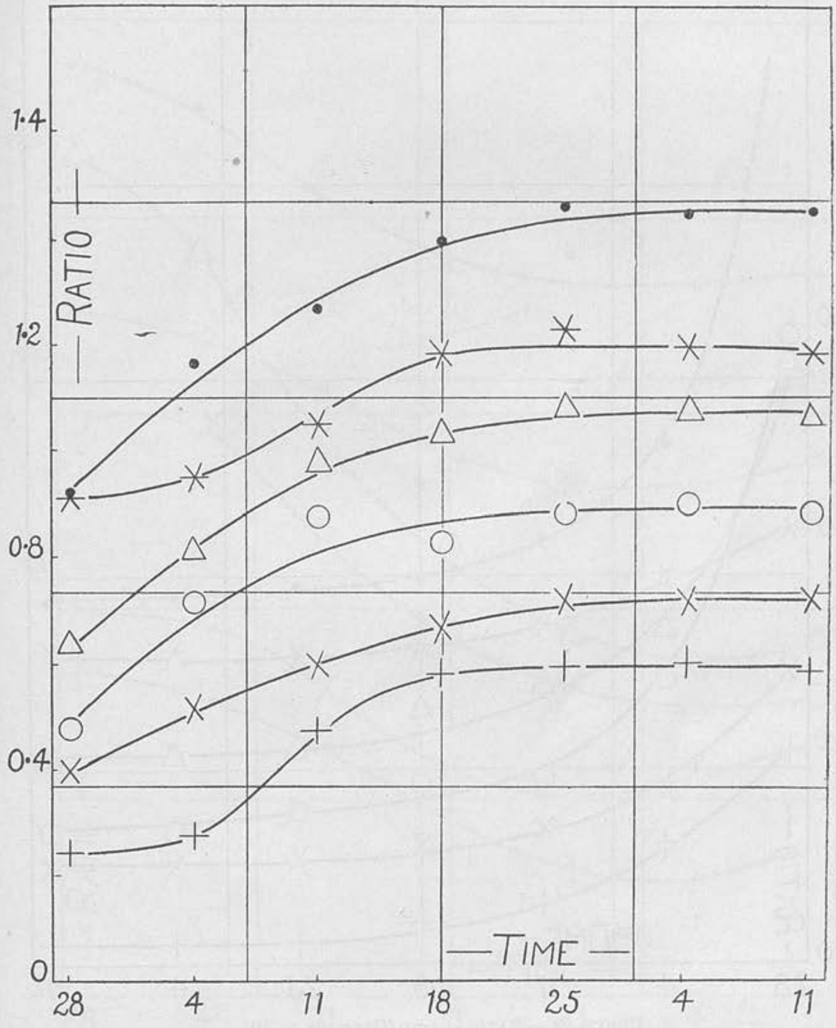


CURVE 26.—YIELD OF ACID PER 100 GRMS.

+ White Hanepoot.	Curve = Yield + 0·5.
× Red Hanepoot.	Curve = Yield + 1·0.
○ Gros Maroc.	Curve = Yield + 2·0.
△ Barbarossa.	Curve = Yield + 3·5.
* Waltham Cross.	Curve = Yield + 4·0.
● Flaming Tokai.	

RATIO: GLUCOSE/TOTAL SOLIDS.

The curves represent the proportion of glucose present when compared with the total solid constituents of the berry. They all indicated the same characteristics. The proportion of glucose increased to a maximum and finally remained practically constant. The onset of the maximum period and the value varied with each grape. It was earliest with Waltham Cross and latest with Flaming Tokai and was in close accordance with the conclusions previously drawn regarding the period of maturity. The value varied between .59 and .67.

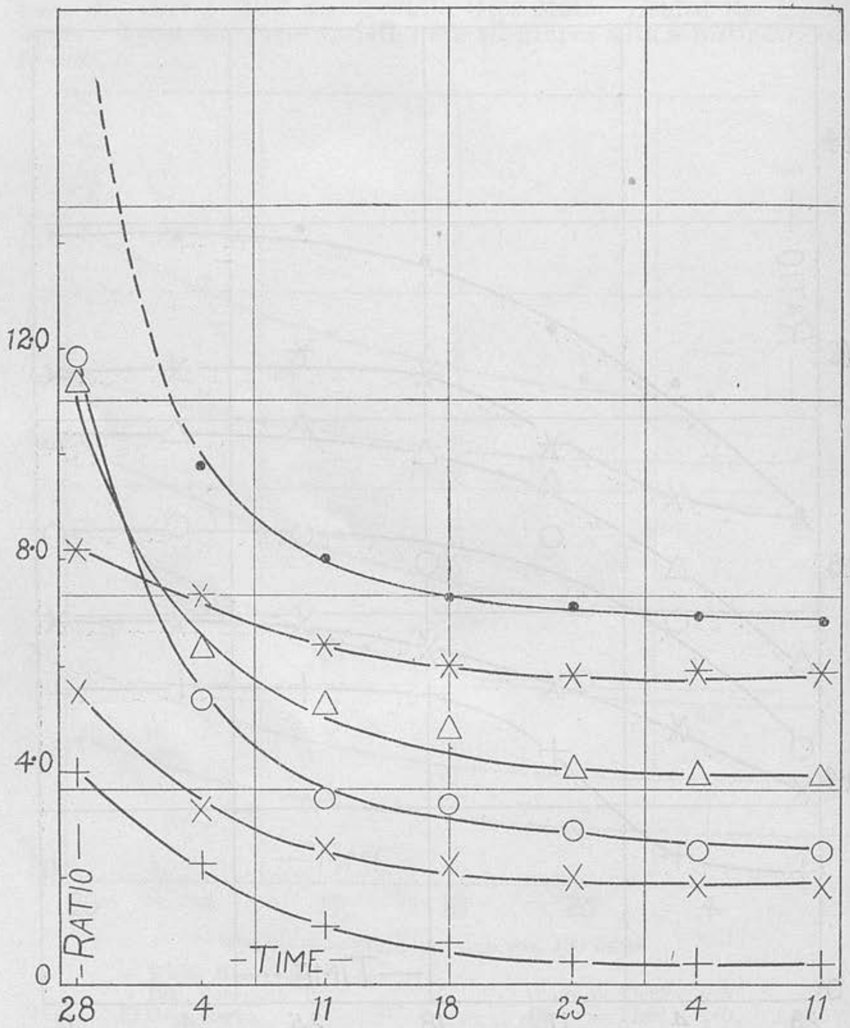


CURVE 27.—RATIO: GLUCOSE/TOTAL SOLIDS.

+ White Hanepoot.
× Red Hanepoot.
○ Gros Maroc.
△ Barbarossa.
* Waltham Cross.
● Flaming Tokai.

Curve = Ratio + 0·10.
Curve = Ratio + 0·25.
Curve = Ratio + 0·40.
Curve = Ratio + 0·55.
Curve = Ratio + 0·80.

It is evident from the curves that at maturity some equilibrium had been reached between the sugar and total solids in the berry and the final portions of the curve represented the limiting factors in this equilibrium. Bioletti, Cruess, and Davi* found that the difference between total solids and sugar became practically constant at maturity. The increase in solids is mainly due to the increase in sugar, and there is practically no conversion of solids into sugar.



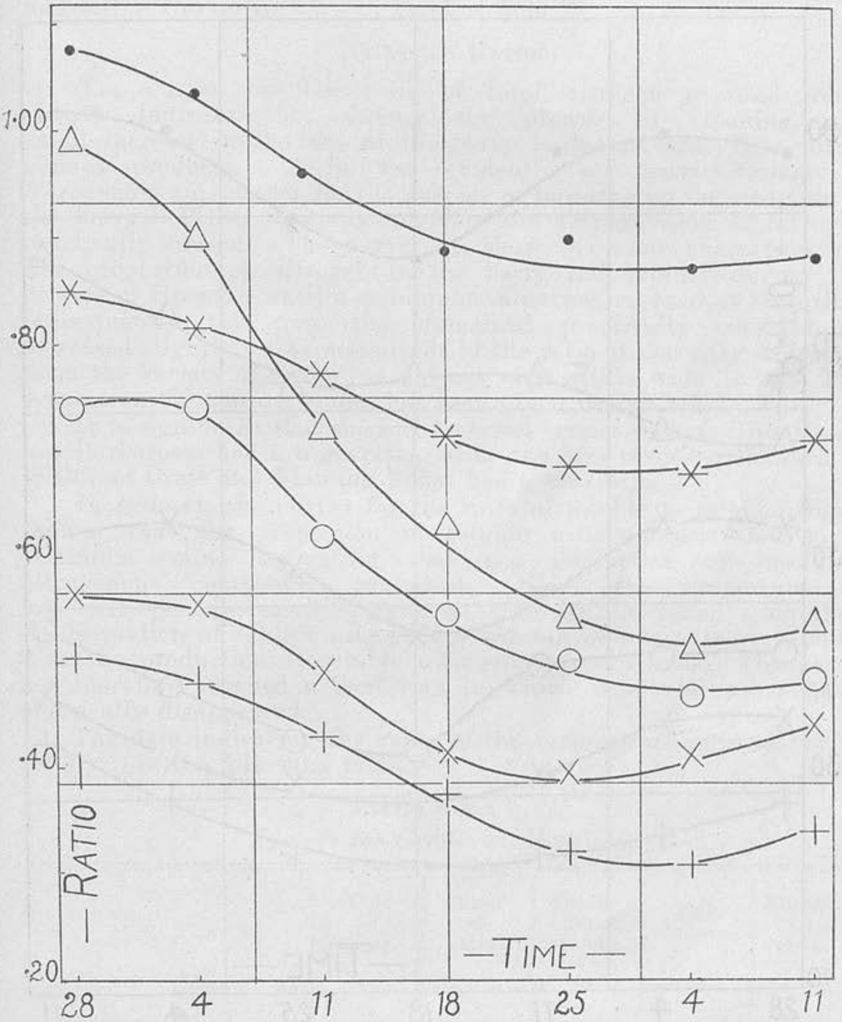
Curve 28.—Ratio: Acid/Glucose × 10.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Ratio + 1·5.
○ Gros Maroc.	Curve = Ratio + 2·0.
△ Barbarossa.	Curve = Ratio + 3·5.
✱ Waltham Cross.	Curve = Ratio + 5·5.
● Flaming Tokai.	Curve = Ratio + 6·5.

* Bioletti, Cruess, and Davi: *Loc. cit.*

The period of maturity from this curve agrees well with that deduced from the other curves, and the figures in Table XXXV may be deduced as representing the equilibrium ratio for each variety.

The figure was smallest for White and Red Hanepoots where the berry was very fleshy, so that the proportion of glucose is smaller (*cf.* Curve XIX.—" Weight of ' Pulp ' "). The figure is high in those berries with small proportion of " pulp."



CURVE 29.—RATIO : TOTAL NITROGEN/TOTAL SOLIDS.

+ White Hanepoot.	
× Red Hanepoot.	Curve = Ratio + 0·10.
○ Gros Maroc.	Curve = Ratio + 0·10.
△ Barbarossa.	Curve = Ratio + 0·20.
* Waltham Cross.	Curve = Ratio + 0·40.
● Flaming Tokai.	Curve = Ratio + 0·60.

F.—SUMMARY AND CONCLUSIONS.

The present investigation confirms the main conclusions of the work carried out in 1923. The scope of the work has, however, been greatly extended. In this case six varieties of grapes have been used, namely, White Hanepoot, Red Hanepoot, Gros Maroc, Barbarossa, Waltham Cross, and Flaming Tokai. From a consideration of the data and the curves drawn from them it was concluded that the grapes were mature about the first week in March. This conclusion agreed very well with that drawn from the taste of the grapes.

Data have been given, indicating approximately the physical nature of the berry when the fruit is mature. It has been found that the volume of juice from a given weight of berries reaches a maximum of between 70-75 per cent. at maturity according to the variety. The soft fleshy berries yielded a lower proportion of juice.

The results of this work, however, all indicate that the changes in the condition of the grapes during ripening depend essentially upon the changes in sugar and acid content of the berry. The sugar increased rapidly during ripening, but at maturity the amount remains very nearly constant or increases only very slowly. The Balling degree of the juice at maturity was about 16°-18°, according to the variety. It has been found that the yield of sugar from a given weight of berries attained a maximum at maturity and remained practically constant. The value depended upon the variety of grape.

It has been found that the changes in total solids which occur after the berry begins to ripen were almost entirely due to the increase in sugar-content, and at maturity there was a definite relationship between the total solids and sugar-content. The value of the ratio between these two quantities varied for each variety but lay between the limits .60-.67. Therefore at maturity the amount of sugar was between 60-67 per cent. of the entire total solids in the berry. The soft fleshy berries had the lower ratio, indicating a lower proportion of glucose.

The acidity decreased during ripening to a minimum value dependent upon the variety of grape, and naturally the hydrogen-ion concentration in the juice increased. The yield of acid from a given weight of grapes showed similar changes, and the minimum value, from .45-.63, was in accordance with the taste of the grape. The ratio of acid to sugar in the juice was found to decrease to a minimum value at maturity, and the value lay between .35 and .50 according to the variety. This figure is slightly higher than that found in the 1923 investigation. The decrease was not in direct inverse proportion to the increase in sugar.

The changes in nitrogen-content were found to be unconnected with the process of ripening in the berry, and it was not possible to predict with any certainty the period of maturity from the nitrogen-content. The only conclusion that can be drawn was that the nitrogenous compounds are connected with the texture of the berry, and it would seem that these compounds are built up from the ammoniacal compounds present in the juice. At maturity the ammoniacal nitrogen is at a minimum.

The mineral-content of the berry increases during ripening, and the absolute amount remains very nearly constant at maturity; and there was some evidence that the mineral-content is connected with the texture of the berry.

The proportion of seeds in the berry decreases during ripening owing to the rapid increase in the pulp of the berry. At maturity the ratio of pulp to seeds becomes very nearly constant. The total solids in the seeds increased during the whole period, and this would seem to be connected with the formation of ligneous and cellulosic bodies when the seeds commence to harden.

When the question of plucking grapes for export purpose is considered, it is clear that two important aspects of the problem become apparent, namely, (*a*) the physical appearance of the berry, (*b*) the quality of the juice.

In the first place the physical aspect of the berry in itself forms an unreliable guide, which will be subject to great variations in individual judgment. It is clear from the data presented that the grapes may be considered ripe before their maximum physical development has been fully attained. Therefore an unnecessary delay of at least a week would be caused by waiting until the berry has attained its maximum size. At the same time, conditions of growth such as climate, soil, thinning of bunches will so alter the appearance of the berry that such a method of judging the maturity of the fruit will become useless. When, however, the appearance and attractiveness of the product are to be considered, this aspect must be given due weight in arriving at a reliable conclusion, although the decision must also depend upon the quality of the juice. For picking, the berry must be large and translucent but still firm, and it would seem the final decision must rest upon individual experience in conjunction with local conditions. Since it has been shown that the berry ripens from the surface inwards, it is clear that the correct judgment, based entirely upon the physical aspect, must be a matter of considerable practical experience.

TABLE XXXVI.

	Degrees Balling.	Acidity.
White Hanepoot	18·0	·75
Red Hanepoot	18·0	·75
Gros Maroc	16·5	·90
Barbarossa	16·0	·70
Waltham Cross	17·0	·70
Flaming Tokai	17·0	·75

However, the problem is simplified when an examination of the juice is carried out, and for rapidity this procedure is the only one which will give reliable information regarding the ripeness of the grape. It has been shown that the most important factors influencing the ripeness of the grape are the sugar and acid content of the juice. The former must be high and the latter low for the best results to be obtained. If the grapes are picked at the period of *initial* maturity, any further changes which occur during storage will have the effect of bringing the berries to full maturity, and this would be the best time to choose. This investigation has shown that this period is reached when the juice has a Balling reading of 16°-18°, according to the variety of grape. If, therefore, the juice expressed from a sufficient number of berries representing an average sample were found to have for each variety a Balling reading of at least that given in Table XXXVI, the grapes could be considered sufficiently mature for export. If also the acidity were determined by titration the amount in such grapes would have to be at most that given in Table XXXVI. For practical purposes these tests would seem to offer the simplest solution of the problem.

To confirm the results, further information could be obtained from the yield of sugar from a given weight of berries and the ratio of acid to sugar. The limits have been given in Table XXXV.

In conclusion, the authors would like to acknowledge the assistance rendered by Mr. Van Reenen, of the Government Wine Farm, who kindly undertook to supply the samples each week as required.

Th. Scot.

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NOTE ON DECREASE IN ACIDITY DURING RIPENING OF GRAPES.

By P. R. v.d. R. Copeman, B.A., B.Sc. D.Sc. 1928

(With two Text-figures.)

The most important factors which determine the quality of a fruit are the sugar and acid content, and in previous work upon the ripening of grapes * it has been shown that the most important changes are those taking place in these two factors. The total acidity, as determined by direct titration of the juice, exhibited a continuous decrease during the periods of investigation. The decrease, however, did not remain uniform, but gradually became less until, at full maturity, the amount of acid remained very nearly constant.

In a paper † on "The Changes in Acid Content of Stored Apples" it has been shown that the acidity of apples decreases during storage, and that the change in acidity follows a logarithmic curve. It was also found that the rate of loss of acidity in apples stored at ordinary temperatures differed from that in apples in cold storage, being greater at the higher temperature. It is clear, therefore, that the changes in acid content under these circumstances is influenced by external conditions such as temperature.

Since there is a decrease in acidity during the ripening of grapes, it was thought that possibly these changes could also be expressed by a logarithmic function. This has been found to be the case, at any rate, during the period of ripening. The observations include the determinations of acidity made in 1923 and 1925 during work upon the ripening of grapes. However, in both cases, the work was commenced at a stage when the initial onset of ripening had started, and there are therefore no data for a comparison to be made with the changes occurring while the amount of acid is increasing.

Tables I. and II. have been taken from the work already mentioned.

* Copeman, "An Investigation into some Physical and Chemical Changes occurring during the Ripening of Grapes," Department of Agriculture Bulletin, Division of Chemistry Series 31, 1924. Copeman and Frater, "Some Physical and Chemical Changes occurring during the Ripening of Grapes," 1925 (unpublished manuscript).

† Haynes, Ann. Bot., 49 (1925), 77.

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TABLE I.

Grapes pressed in 1923.

Acidity as Grammes of Tartaric Acid per 1000 *c.c. Juice.*

Date.	Days.	White Hanepoot.	Red Hanepoot.	Barbarossa.	Flaming Tokai.
31.1.23	0	..	19·2	..	..
7.2.23	7	14·4	9·9	12·5	15·6
14.2.23	14	11·4	10·6	12·4	12·9
21.2.23	21	8·5	8·8	9·3	12·1
28.2.23	28	7·6	6·8	7·8	9·2
7.3.23	35	6·8	5·4	6·6	7·0
14.3.23	42	5·6	5·4	6·1	6·2
21.3.23	49	4·9	4·5	4·7	6·0
28.3.23	56	5·2	4·4	4·5	4·4

TABLE II.

Grapes pressed in 1925.

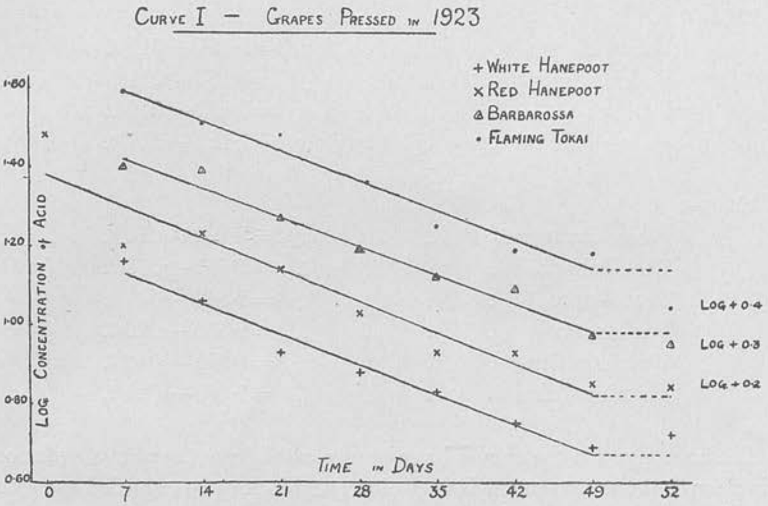
Acidity as Grammes of Tartaric Acid per 1000 *c.c. Juice.*

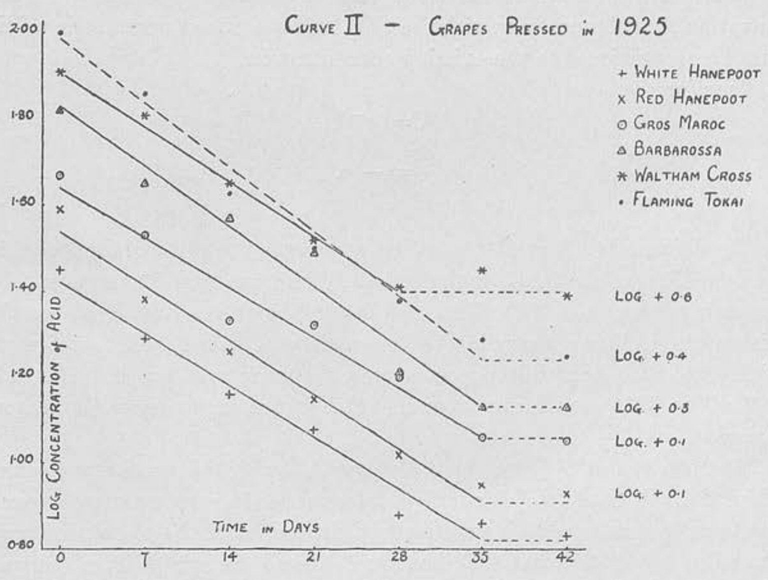
Date.	Days.	White Hanepoot.	Red Hanepoot.	Gros Maroc.	Barbarossa.	Waltham Cross.	Flaming Tokai.
28.1.25	0	28·1	31·0	37·2	33·1	20·4	40·2
4.2.25	7	19·3	19·1	26·8	22·5	16·1	28·8
11.2.25	14	14·5	14·5	17·1	18·4	11·1	16·9
18.2.25	21	12·0	11·3	16·7	15·3	8·3	12·5
25.2.25	28	7·6	8·4	12·5	8·1	6·4	9·6
4.3.25	35	7·3	7·0	9·1	6·7	7·0	7·7
11.3.25	42	6·8	6·7	9·0	6·7	6·2	7·0

When the logarithms of the concentration are plotted against the time, a straight line is obtained as shown in Curves I. and II. Therefore the changes in acidity may be expressed by means of the curve

$$\log C = a - bt.$$

It was found, however, that if the last reading were neglected, when the constants of the equation were calculated from the data, much closer





agreement was obtained between the observed and calculated readings. In the case of Waltham Cross the last two readings have been neglected in the calculation. The most suitable curves have been calculated by the method of least squares and the following results obtained :—

1923—

White Hanepoot . .	$\log C = 1{\cdot}127 - {\cdot}011\,t.$
Red Hanepoot . . .	,, $= 1{\cdot}180 - {\cdot}011\,t.$
Barbarossa . . .	,, $= 1{\cdot}123 - {\cdot}010\,t.$
Flaming Tokai . . .	,, $= 1{\cdot}195 - {\cdot}011\,t.$

1925—

White Hanepoot . .	$\log C = 1{\cdot}422 - {\cdot}017\,t.$
Red Hanepoot . . .	,, $= 1{\cdot}441 - {\cdot}018\,t.$
Gros Maroc . . .	,, $= 1{\cdot}542 - {\cdot}017\,t.$
Barbarossa . . .	,, $= 1{\cdot}530 - {\cdot}020\,t.$
Waltham Cross . . .	,, $= 1{\cdot}311 - {\cdot}018\,t.$
Flaming Tokai . . .	,, $= 1{\cdot}585 - {\cdot}021\,t.$

The lines given in the curves have been plotted from the above equations. It is clear that the agreement is very close, and it may be regarded as certain that the change in acidity during the period of observation may be expressed by means of a logarithmic function. Under these circumstances the concentration of acid must vary with the time, and the rate of decrease in acidity must be proportional to the existing concentration.

Therefore

$$C = ke^{-bt}$$

$$\frac{dc}{dt} = -bc.$$

The constant " a " in the equations represents the value of the logarithm of the acidity at the time at which the experiments were commenced. On comparing the values of " a " in each set among themselves, it is seen that this constant differs according to the variety of grape, and therefore the acidity at any given time depends upon the variety of grape. The value of " a " in 1923 was lower than in 1925, indicating a probable seasonal variation.

The constant " b " measures the rate at which the acidity declines. When the values of " b " for individual varieties in each set are compared, it is seen that this value is practically independent of the variety of grape. The value for 1923 (about ·01), however, differed materially from the value (about ·02) for 1925. This again suggests that the decrease in acidity is dependent upon the season. Since the decrease in acidity of grapes is closely related to the ripening of the fruit, it seems clear that the rate at which the fruit ripens depends upon some seasonal variation. At the same time it would appear that the rate of ripening during any season is independent of the variety of grape.

On examination of the curves it is seen that the lines lie very close to the mean position of the points in every case until the end of the period, when the calculated slope becomes too steep and the curve begins to flatten out. At this stage the decrease in acidity becomes negligible and the acidity remains very nearly constant. On further comparison it was found that this stage corresponded with the time at which the fruit could be regarded as ripe. Therefore at maturity it would appear that there is little or no further decrease in acidity. This is particularly noticeable in the case of Waltham Cross, in which the stage of maturity was reached about a week earlier than in the case of the remaining varieties.

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